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(54) Title: STERICALLY STABILIZED SECOND-ORDER NONLINEAR OPTICAL CHROMOPHORES AND DEVICES INCORPORATING THE SAME

(57) Abstract: Sterically stabilized second-order nonlinear optical chromophores and devices incorporating the same are embodied in a variety of chromophore materials. An exemplary preferred chromophore includes an electron donor group, an electron acceptor group and a bridge structure therebetween, with the electron acceptor group being double bonded to the bridge structure. In a preferred embodiment, the bridge structure also includes at least one bulky side group. Another exemplary preferred chromophore includes an electron donor group, an electron acceptor group and a ring-locked bridge structure between the electron donor group and the electron acceptor group. The bridge structure comprises, for example, two protected alicyclic rings or ring-locked trienone. Another exemplary preferred chromophore includes an electron donor group, a ring-locked tricyano electron acceptor group, and a bridge structure therebetween. In a preferred embodiment, the electron acceptor group comprises an isophorone structure. Another exemplary preferred chromophore includes an electron donor group, an electron acceptor group, and a bridge structure therebetween, with the bridge structure including a bithiophene unit. In a preferred embodiment, the bridge structure further includes a modified isophorone unit.

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STERICALLY STABILIZED SECOND-ORDER NONLINEAR OPTICAL
CHROMOPHORES AND DEVICES INCORPORATING THE SAME

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH AND

5 DEVELOPMENT

This invention was made with support from the government of the United States of America under Contracts F49620-97-C-0064, F49620-97-1-0307, F49620-97-1-0491, F49620-97-C-0064, F49620-98-C-0059, F49620-98-C-0077, 10 F49620-99-0040 awarded by the United States Air Force. The government of the United States of America has certain rights in this invention as provided by these contracts.

BACKGROUND OF THE INVENTION

15 Field of the Invention

The present invention relates to nonlinear optical chromophores and, more particularly, pertains to sterically stabilized second-order nonlinear optical chromophores and devices incorporating the same.

20

Description of the Related Art

Organic second-order nonlinear optical (NLO) materials have received increasing attention for applications involving signal processing and 25 telecommunications. One of the challenges in this field is to design and synthesize second-order NLO chromophores (the active components of second-order nonlinear optical materials) that simultaneously possess large first molecular hyperpolarizabilities (β), good chemical and 30 thermal stability, and optical transparency at optical communication wavelengths (1.3 and 1.55 μm). Chromophore intermolecular electrostatic interactions prevent the simple scaling of molecular optical nonlinearity into macroscopic optical nonlinearity. Such interactions

strongly attenuate the efficient induction of acentric chromophore order (hence, electrooptic activity) by electric field poling or self-assembly methods. Chromophores with β values many times those of the well-known Disperse Red 19 dye are thus required to obtain electrooptic coefficients comparable to or higher than those of the leading commercial material crystalline lithium niobate.

The value of β for a chromophore can be increased by using a diene moiety in place of thiophene in the conventional phenylethylenethiophene π -conjugated bridge. Moreover, this enhancement in β can be accomplished without an increase in the wavelength of the charge-transfer absorption λ_{\max} . However, the resulting phenylpolyene bridge has poor thermal stability unless the polyene structure is sterically protected. The synthesis of various sterically-protected (ring-locked) phenylpolyene chromophores involves cyclic enones such as isophorone, verbenone and double-ring locked dienone as starting materials and intermediates. The Knoevenagel coupling reaction between enones and electron acceptors is the critical step in both backward and forward methods reported. The low reactivity of enone severely limits the choice of acceptor to only a few molecules including malononitrile, isoxazolone, and thiobarbituric acid and therefore has become the bottleneck in the development of ring-locked phenylpolyene-bridged high β chromophores.

SUMMARY OF THE INVENTION

A new class of ring-locked aminophenylpolyenal donor-bridges has been developed. These new donor-bridges, according to the present invention, have very high Knoevenagel reactivity and have been coupled with a variety

of acceptors bearing acidic methyl or methylene groups (including the most desired TCF and TCI type of acceptors shown in Figure 11) to obtain a new class of second-order NLO chromophores. This methodology broadens the scope of
5 polyene-bridged chromophores without significantly sacrificing thermal stability or optical transparency. This synthetic approach leads to the development of device-quality NLO chromophores (shown in Figure 1) possessing $\mu\beta$ values (where μ is the chromophore dipole
10 moment) of $15,000 \times 10^{-48}$ esu or greater at $1.9 \mu\text{m}$ as determined by the electric field induced second harmonic generation (EFISH) technique.

A variety of different molecular structures are possible for the chromophores of the present invention. An
15 exemplary preferred chromophore according to the present invention includes an electron donor group, an electron acceptor group and a bridge structure therebetween, with the electron acceptor group being double bonded to the bridge structure. In a preferred embodiment, the bridge
20 structure also includes at least one bulky side group.

Another exemplary preferred chromophore according to the present invention includes an electron donor group, an electron acceptor group and a ring-locked bridge structure between the electron donor group and the electron acceptor
25 group. The bridge structure comprises, for example, two protected alicyclic rings or ring-locked trienone.

Another exemplary preferred chromophore according to the present invention includes an electron donor group, a ring-locked tricyano electron acceptor group, and a bridge
30 structure therebetween. In a preferred embodiment, the electron acceptor group comprises an isophorone structure.

Another exemplary preferred chromophore according to the present invention includes an electron donor group, an

electron acceptor group, and a bridge structure therebetween, with the bridge structure including a bithiophene unit. In a preferred embodiment, the bridge structure further includes a modified isophorone unit.

5 The NLO materials of the present invention are suitable for a wide range of devices. Functions performed by these devices include, but are not limited to, the following: electrical to optical signal transduction; radio
10 wave to millimeter wave electromagnetic radiation (signal) detection; radio wave to millimeter wave signal generation (broadcasting); optical and millimeter wave beam steering; and signal processing such as analog to digital conversion, ultrafast of signals at nodes of optical networks, and
15 highly precise phase control of optical and millimeter wave signals.

DESCRIPTION OF THE DRAWINGS

Other objects, features and advantages of the invention will become readily apparent upon reference to
20 the following detailed description when considered in conjunction with the accompanying drawings, in which like reference numerals designate like parts throughout the figures thereof, and wherein:

FIG. 1 illustrates the basic structure of CLD, GLD and
25 ZLD chromophores according to the present invention;

FIG. 2 illustrates exemplary preferred CLD chromophores according to the present invention;

FIG. 3 illustrates an exemplary preferred method according to the present invention for synthesizing a CLD
30 chromophore;

FIG. 4 illustrates exemplary preferred CLD chromophores with alkyl derivative at the middle ring;

FIG. 5 illustrates an exemplary preferred method according to the present invention for synthesizing a sterically modified CLD chromophore;

FIG. 6 illustrates an exemplary preferred method according to the present invention for synthesizing a GLD chromophore;

FIG. 7 illustrates an exemplary preferred method according to the present invention for synthesizing a ZLD chromophore;

FIG. 8 illustrates exemplary preferred chromophores containing bithiophene units and modified isophorone units according to the present invention;

FIG. 9A illustrates the synthesis, thermal, and optical properties of chromophores incorporating bithiophene units according to the present invention;

FIG. 9B illustrates an exemplary preferred synthetic scheme for the chromophore of FIG. 9A;

FIG. 10 illustrates an exemplary preferred method of bridge modification by bithiophene insertion and isophorone modification according to the present invention;

FIG. 11 illustrates exemplary preferred ring-locked tricyano electron acceptors for the chromophores according to the present invention;

FIG. 12 illustrates a version of CLD chromophore according to the present invention where the cyanofuran acceptor has been modified by replacement of the furan oxygen atom with a isophorone structure;

FIG. 13 illustrates exemplary preferred alternative donor structures for the FTC, CLD and GLD chromophores according to the present invention;

FIGs. 14A and 14B illustrate exemplary preferred FTC chromophores with modified donor structures according to the present invention;

FIG. 15 illustrates the preparation of an exemplary preferred CLD-containing polyester polymer according to the present invention;

FIG. 16 illustrates the variation of electrooptic activity (divided by molecular polarizability) versus chromophore concentration in the polymer lattice for two values of the electric poling field;

FIG. 17 illustrates an exemplary preferred electrooptic device employing a constant electric field bias, the device incorporating a chromophore material the present invention;

FIG. 18 illustrates an exemplary preferred Mach Zehnder modulator incorporating a chromophore material of the present invention; and

FIG. 19 illustrates the use of a chromophore material of the present invention (in the form of microstrip lines) in a microwave phase shifter of the type employed in optically controlled phased array radars.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following is a detailed description of the best presently known mode of carrying out the invention. This description is not to be taken in a limiting sense, but is made merely for the purpose of illustrating the general principles of the invention.

This application is a continuation-in-part of U.S. patent application serial number 09/122,806 entitled "New Class of High Hyperpolarizability Organic Chromophores and Process for Synthesizing the Same" filed on July 27, 1998,

the disclosure of which is incorporated herein by reference in its entirety.

Referring to FIG. 1, three molecular chromophore structures according to the present invention are identified by their abbreviated names: CLD, GLD and ZLD. Each chromophore includes an electron donor group ("D"), an electron acceptor group ("A") and a bridge structure therebetween. As shown in FIG. 1, in the exemplary preferred chromophores, the electron acceptor group is connected to the ring-locked polyene bridge structure with a conjugated diene. See, C. Zhang, A. S. Ren, F. Wang, J. Zhu, L. Dalton, "Synthesis and Characterization of Sterically Stabilized Second-Order Nonlinear Optical Chromophores", Chem. Mater. 1999, 11, 1966-1968, which is incorporated herein by reference. Within the scope of the present invention, it is also contemplated that the electron donor group can be double bonded to the bridge structure.

Exemplary preferred structures for the electron donor group are shown in FIGs. 1 and 13. In FIG. 1, R_1 to R_9 = H, $-C_nH_{2n+1}$, $n = 1-30$ including primary, secondary, tertiary and any branched alkyl groups, or any alkyl group with 1-30 carbon atoms functionalized with one or more of the following functional groups: hydroxy, ether, ester, amino, silyl, siloxy.

Exemplary preferred structures for the electron acceptor group are shown in FIG. 11. The electron acceptor groups preferably have five-member or six-member rings. However, rings with seven or more members can also be employed.

Generally, it has been observed that dipole moment and molecular hyperpolarizability increase from CLD to ZLD. Final device performance (electrooptic activity) is

related to the product of dipole moment and hyperpolarizability. A corresponding increase in electrooptic activity over this series has also been observed. For example, for measurements carried out at 5 1.06 microns wavelength, the following electrooptic activities coefficients were observed: 55 pm/V (FTC), 85 pm/V (CLD), 110 pm/V (GLD). These values were obtained for the low dielectric polymer matrix poly-(methymethacrylate), PMMA. Somewhat larger electrooptic 10 coefficients were observed in polymer matrices (e.g., amorphous poly(carbonate), APC) of higher dielectric constant.

A large number of variations of the CLD, GLD and ZLD structures have been synthesized, characterized, and 15 utilized in the fabrication of prototype devices by modifying the starting materials in the general synthetic schemes presented herein and in U.S. patent application serial number 09/122,806. Exemplary preferred CLD chromophores are shown in FIG. 2.

20

Synthesis of CLD Chromophore

Referring to FIG. 3, an exemplary preferred method for synthesizing CLD is illustrated. The exemplary preferred method for synthesis is described below.

25 A mixture of 1.815 mol of p-N,N-bis(2-hydroxyethyl)aminobenzaldehyde, 2.178 mol, 301g of isophorone, 1L of EtOH, and 2.1 mol of sodium ethoxide was stirred at 50 °C for 15h. The reaction was stopped by adding 50 g of water. Ethanol was evaporated in vacuo and 30 product crystallized out. The product was collected by filtration, washed with water. It was vacuumed to remove water and then recrystallized from EtOAc to give 90% yield. Mass: 329.200, found 329.199.

TBDMS protection: A mixture of 45.4g, 138mmol of the above product, 80g DMF, 42g imidazole and 46g t-butyldimethylsilyl chloride was stirred at 60 °C for 6h. The mixture was then poured to water and extracted with 5 hexane. The extract was condensed and the residual was purified by column chromatography to give 72.7g product: 94.5% yield. Crystals from hexane had a melting point of 106.5-108 °C. Elemental analysis: calc. C 68.88, H 9.94, N 2.51. Found C 69.04, H 9.92, N 2.48.

10 Extension of ketone to aldehyde: A solution of 110mmol, 13.77g of N-cyclohexylacetimine in 35ml THF was added to 77ml 1.5M LDA/cyclohexane at -50C. After the addition the mixture was warmed up with an ice bath and then recooled to -78C. A solution of 61.35g of the above 15 ketone in 105ml THF was added. The mixture was then warmed up in air and then acidified with dilute acetic acid solution and stirred at room temperature for 11h. After usual work up, the crude product was purified by column chromatography to give 26.56g pure product: 41.6% yield.

20 CLD-1: A mixture of 10.99g of above aldehyde, 3.75g of 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran, 110ml anhydrous EtOH, 0.7ml of 21wt% EtONa/EtOH was refluxed for 4 h. The product was collected by filtration and recrystallized from ethanol to 25 give 11.5g chromophore: 80% yield. Elemental analysis: calcd.: C 70.63, H 8.43, N 7.32. Found: C 70.66, H 8.53, N 7.36. λ_{\max} : 632.4nm in dioxane, 692.2nm in CHCl₃. Td 274.7 °C by DSC (N₂, 10 °C/min).

A protonated version is synthesized by removing the 30 TBDMS protecting group. A number of variants of this structure have been synthesized by use of modified starting materials following the general reaction scheme presented above.

Variations to the chromophores have been made to improve electrooptic activity either by sterically inhibiting unwanted intermolecular electrostatic interactions, by improving the electron-withdrawing characteristics of the acceptor end of the chromophores, 5 by improving the electron donating characteristics of the donor end of the chromophore, or by improving electron communication of the bridge segment of the chromophore.

Referring to FIG. 4, a representative example of 10 steric modification of the bridge segment of the CLD chromophore shows the addition of a bulky side group (alkyl derivative at the middle ring) to reduce electrostatic interaction. It should be understood, however, that other side groups can be added. A plurality 15 of bulky side groups, e.g., branched or tertiary side groups, can also be added to each bridge segment.

Synthesis of Sterically Modified CLD Chromophore

An exemplary preferred method for synthesizing a 20 sterically modified CLD chromophore is illustrated in FIG. 5. The exemplary preferred method for synthesis is described below.

2-Hexyl-isophorone: This compound was synthesized according a literature method (Stork, G. Benaim, J. J. 25 *Am. Chem. Soc.* 1971, 5938-5939.) from isophorone in 55% yield. ^1H NMR (CDCl_3): δ 2.29 (t, 6.32 Hz, 2H), 2.23 (s, 2H), 1.92 (s, 2H), 1.30 (m, 8H), 1.00 (s, 6H), 0.88 (t, 6.42 Hz, 3H). ^{13}C NMR (CDCl_3): δ 198.55, 151.93, 134.53, 51.16, 46.75, 32.43, 31.56, 29.25, 28.90, 27.99, 24.80, 30 22.41, 21.04, 13.88. . Anal. Calcd. for $\text{C}_{15}\text{H}_{26}\text{O}$: C, 81.02; H, 11.79; Found: C, 81.18; H, 11.87.

3-[p-N,N-Bis(2-t
butyldimethylsiloxyethyl)aminostyryl]-5,5-dimethyl-2-

hexyl-cyclohex-2-enone: Potassium t-butoxide (30.32 g, 97%, 0.262 mol.) was added to a solution of p-N,N-Bis(2-t-butyldimethylsiloxyethyl)aminobenzaldehyde (, 53.4 g, 0.122 mol.) and 2-hexyl-isophorone (compound 10, 26.6 g, 0.118 mol.) in diglyme (200 mL, KOH dried) over 3 min. Ice bath was used to keep the temperature below 50 °C. The reaction mixture was stirred at room temperature for 25 min. and then was poured to dilute acetic acid (0.28 mol HOAc in 200 mL of water). The extra acid was neutralized saturated aqueous sodium bicarbonate. The organic layer was separated, washed with water, dried with magnesium sulfate and rotovapped to dryness. The residue was purified by a silica gel column using ethyl acetate/hexane (1/20, v/v) to afford 8.33 g red thick oil: yield 22% based on reacted starting material. Only about starting materials reacted. ¹H NMR (CDCl₃): δ 7.36 (d, 8.81 Hz, 2H), 7.14 (d, 16.06 Hz, 1H), 6.88 (d, 16.09 Hz, 1H), 6.69 (d, 8.91 Hz, 2H), 3.78 (t, 6.06 Hz, 4H), 3.56 (t, 5.89 Hz, 4H), 2.53 (br, 2H), 2.48 (s, 2H), 2.29 (s, 2H), 1.33 (m, 8H), 1.05 (s, 6H), 0.90 (s, 18H), 0.04 (s, 12H) ppm. ¹³C NMR (CDCl₃): δ 198.87, 148.41, 147.67, 134.47, 134.19, 128.52, 124.38, 121.71, 111.54, 60.21, 53.42, 51.37, 39.82, 32.27, 31.65, 29.90, 29.37, 28.39, 25.79, 24.30, 22.54 ppm.

TBDMS protected, hexyl derivatized donor-bridge): A solution of lithium diisopropylamine (4.7 mL 1.5M in THF, 7.05 mmol.) in THF (12 mL) was cooled to -20 °C. N-cyclohexylacetimine (6.7 mmol.) was added and the mixture was allowed to warm up to 0 °C and was kept at the temperature for 15 min. It was re-cooled to -20 °C and 3-[p-N,N-Bis(2-t-butyldimethylsiloxyethyl)aminostyryl]-5,5-dimethyl-2-hexyl-cyclohex-2-enone (4.31g, 6.71 mmol., in 15 mL of THF) was added over 3 min. It was stirred for 5

more min. and was stopped by adding 1N acetic acid solution. The product was extracted with hexane and the extract was washed with sodium bicarbonate solution, dried with magnesium sulfate and rotovapped to dryness. The residue was purified by a silica gel column using ethyl acetate/hexane (1/20, v/v) to afford 0.55g red oil product and recovered 3.45g starting material. The yield was 61% based on consumed starting ketone. ^1H NMR (CDCl_3): δ 10.13 (d, 8.22 Hz, 1H), 7.33 (d, 8.80 Hz, 2H), 7.15 (d, 15.54 Hz, 1H), 6.77 (d, 16.38 Hz, 1H), 6.68 (d, 9.13 Hz, 2H), 6.20 (d, 7.94 Hz, 1H), 3.78 (t, 5.84 Hz, 4H), 3.55 (t, 5.74 Hz, 4H), 2.68 (s, 2H), 2.52 (br, t, 2H), 2.38 (s, 2H), 1.34 (m, 8H), 1.01 (s, 6H), 0.89 (s, 18H), 0.04 (s, 12H) ppm. ^{13}C NMR (CDCl_3): δ 191.53, 157.46, 148.14, 140.57, 133.16, 132.65, 128.23, 124.87, 123.47, 122.31, 111.59, 60.23, 53.43, 40.40, 39.38, 31.59, 30.15, 29.78, 29.52, 28.22, 27.26, 25.79, 22.57, 18.15, 14.03, -5.47 ppm. Exact mass calcd. for $\text{C}_{40}\text{H}_{69}\text{N}_1\text{O}_3\text{Si}_2$: 668.493. Found: 668.489.

Chromophore: Above aldehyde (0.55g, 0.823 mmol.) and 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (0.198g, 0.988 mmol.) were dissolved in 5 mL of ethanol that contained 7 mg of sodium hydroxide. The solution was refluxed for 3.5 hours and then 10 mL of water was added dropwise to precipitate out the product. The crude product was collected by filtration, washed with water, dried in vacuo, and purified by a silica gel column using ethyl acetate/hexane (1/7 to 1/5, v/v) to give 245 mg pure product: yield 35%. ^1H NMR (CDCl_3): δ 8.06 (q, $J_1 = 12.02$ Hz, $J_2 = 14.74$ Hz, 1H), 7.36 (d, 8.89 Hz, 2H), 7.22 (d, 16.29 Hz, 1H), 6.88 (d, 15.79 Hz, 1H), 6.70 (8.78 Hz, 2H), 6.63 (d, 12.09 Hz, 1H), 6.35 (d, 14.96 Hz, 1H), 3.78 (t, 5.77 Hz, 4H), 3.57 (d, 5.83 Hz, 1H), 2.61 (br, t, 2H),

2.44 (s, 4H), 1.71 (s, 6H), 1.43 (br, m, 8H), 0.89 (s, 18H), 0.03 (s, 12H) ppm. ^{13}C NMR (CDCl_3): δ 176.35, 173.46, 155.48, 148.88, 145.13, 144.08, 135.16, 134.78, 128.94, 124.92, 124.27, 122.39, 115.82, 112.80, 112.06, 5 111.90, 111.77, 96.78, 93.93, 60.40, 55.68, 53.57, 40.87, 40.71, 31.78, 30.64, 30.18, 29.72, 28.43, 27.25, 26.70, 25.97, 22.76, 18.35, 14.24, -5.28 ppm. Exact mass calculated for $\text{C}_{51}\text{H}_{76}\text{N}_4\text{O}_3\text{Si}_2$: 848.543. Found: 848.546.

In addition to the hexyl variant shown, other linear
10 and branched alkyl derivatives were synthesized and characterized. Also, the methyl groups on the isophorone alicyclic ring were replaced by a variety of longer alkyl groups. Both hydroxylated (deprotected) and TBDMS protected donor structures were prepared, characterized
15 and utilized.

Synthesis of GLD Chromophore

Referring to FIG. 6, an exemplary preferred method for synthesizing the GLD chromophore is illustrated. The
20 exemplary preferred method for synthesis is described below.

The procedure for synthesizing GLD is essentially the same as the CLD synthesis procedure shown in FIG. 3, except that two steps were added to construct the fused ring
25 system. The discussion of FIG. 3 is applicable with respect to the preparation of variants of this theme.

Synthesis of ZLD Chromophore

Referring to FIG. 7, an exemplary preferred method for
30 synthesizing the ZLD chromophore is illustrated. The exemplary preferred method for synthesis is described below.

Synthesis of ring-locked trienone: To a solution of 11mmol of the starting material (synthesized according C.-F. Shu et al, Chem. Mater. 1998, 10, 3284) in 20ml of anhydrous THF and 1.3eq cooled in ice bath, 4.77ml 3M methylmagnesium bromide ether solution was added over 2 min. After addition, the mixture was refluxed for 30min. The mixture was acidified with 30wt% aqueous acetic acid solution and stirred at room temperature overnight. After usual work up, the crude product was purified using to give 1.37g pure product, yield 52%. Recrystallization from hexane gave orange red crystals with a mp of 135.5-137.5C. Elemental analysis: Calcd. for C₁₇H₂₂O: C 84.25; H 9.15;. Found: C 83.96, H 9.25.

The remaining steps are similar to those shown in FIG. 3.

Referring to FIG. 8, exemplary preferred chromophores according to the present invention include bridge structures which have been modified by the insertion of bithiophene units and modified isophorone units. The synthesis, thermal, and optical properties of chromophores incorporating bithiophene units are shown in FIG. 9A. As illustrated, this modification provides an increased thermal stability characteristic.

Synthesis of Chromophore Incorporating Bithiophene Units

Referring to FIG. 9B, an exemplary preferred method for synthesizing the chromophore incorporating bithiophene units is illustrated. The exemplary preferred method for synthesis is described below.

3,3',5,5'-Tetrabromo-2,2'-bithiophene. Bromine (41.2 g, 257.8 mmol) was added dropwise to a solution of 2,2'-bithiophene (10 g, 60.2 mol) in 250 ml of chloroform at 0-

5 °C. A light-yellow solid was formed gradually during the addition. The mixture was stirred at room temperature overnight and then refluxed for 2 h. After cooling to room temperature, 100 ml of 10% KOH aqueous solution was added. The resulting mixture was extracted with chloroform to give the crude product. Recrystallization from ethanol/CHCl₃ (1:1) afforded a light-yellow crystal in the yield of 87 % (25.1 g). ¹H-NMR (CDCl₃, ppm): δ 7.05 (s, 2H).

10 3,3'-Dibromo-2,2'-bithiophene. A mixture of 3,3',5,5'-tetrabromo-2,2'-bithiophene (25 g, 52.3 mmol), ethanol (50 ml), water (50 ml) and glacial acetic acid (100 ml) was heated to reflux. Then the heating oil bath was removed, and zinc powder (13.1 g, 200 mmol) was added in portions at such a rate that the mixture continued to reflux. After the addition was complete, heating was continued, the mixture was refluxed for another 5 h and cooled down to room temperature. The unreacted zinc powder was filtered off and the filtrate was collected, diluted with diethyl ether and then washed twice with water. The ether solution was dried with anhydrous MgSO₄ and the solvent was evaporated under reduced pressure. The crude product was recrystallized from hexane to afford a greenish crystal in the yield of 91 % (15.3 g). ¹H-NMR (CDCl₃, ppm): δ 7.40 (d, 2H, J=5 Hz), 7.11 (d, 2H, J=5 Hz).

25 3,3'-Dihexyl-2,2'-bithiophene. Hexylmagnesium bromide (100 ml, 2 M solution in diethyl ether, 200 mol) was added dropwise to a solution of 3,3'-dibromo-2,2'-bithiophene (15 g, 46.6 mmol) and Ni(dppp)Cl₂ (0.5 g, 0.1 mmol) in 100 ml of diethyl ether at 0 °C. The reaction was slightly exothermic and a red brown coloration was observed. After stirred and heated for 24 h, the reaction mixture was cautiously poured into a mixture of crushed ice and

diluted HCl solution and extracted with ether. The combined extracts were dried over anhydrous MgSO_4 and filtered. After removal of the solvent, the residue was vacuum-distilled to give a clear viscous oil (15.6 g, 81 %). $^1\text{H-NMR}$ (CDCl_3 , ppm): δ 7.25 (d, 2H, $J=5$ Hz), 6.96 (d, 2H, $J=5$ Hz), 2.50 (t, 4H), 1.54 (m, 4H), 1.23 (m, 12H), 0.85 (t, 6H).

5-(3,3'-Dihexyl-2,2'-bithienyl)methylphosphonate. A solution of 3,3'-dihexyl-2,2'-bithiophene (8 g, 24 mmol) in 80 ml of anhydrous THF was added over 45 min under argon at -78°C to a stirred solution of *n*-butyllithium (9.6 ml, 2.5 M in hexanes, 24 mmol) in 150 ml of THF. The solution was stirred for 45 min at -78°C , and then transferred, via cannula, into a flask cooled to -20°C in a dry ice/ CCl_4 bath, containing CuI (4.6 g, 24 mmol). After 2 h, diethyl iodomethylphosphonate (6.7 g, 24 mmol) was added in one portion, and the solution was reacted at room temperature overnight. The dark reaction mixture was poured into 300 ml of ether and 200 ml of water, and the organic layer washed successively with 3x200 ml water, 1x200 ml 5% aqueous NaHCO_3 , 2x200 ml water, and 2x200 ml saturated brine solution. The organic layer was dried (MgSO_4), and evaporated. The resulting residue was purified by column chromatography packed with silica gel (1:1 hexanes: ethyl acetate), affording a clear yellow viscous oil (7.2 g, 62 %). $^1\text{H-NMR}$ (CDCl_3 , ppm): δ 7.26 (d, 1H, $J=5$ Hz), 6.96 (d, 1H, $J=5$ Hz), 6.88 (d, 1H, $J=3.2$ Hz), 4.12 (m, 4H), 3.34 (d, 2H, $J=20.5\text{Hz}$), 2.47 (m, 4H), 1.52 (m, 4H), 1.31 (t, 6H), 1.24 (m, 12H), 0.86 (t, 6H).

5-(5'-Bromo-3,3'-dihexyl-2,2'-bithienyl)methylphosphonate. A solution of 5-(3,3'-dihexyl-2,2'-bithienyl)methylphosphonate (7 g, 14.5 mmol) and NBS (2.8 g, 15.7 mmol) in 150 ml of dichloromethane

was stirred at 0 °C for 1 h and at room temperature for 2 h. Then the mixture was washed with 100 ml of 10 % KOH aqueous solution and then with water until the solution was neutral. The organic layer was concentrated to give
5 the crude product (7.8 g, 96 %). ¹H-NMR (CDCl₃, ppm): δ 6.90 (s, 1H), 6.84 (d, 1H, J=5 Hz), 4.10 (m, 4H), 3.30 (d, 2H, J=20.5Hz), 2.43 (m, 4H), 1.50 (m, 4H), 1.29 (t, 6H), 1.22 (m, 12H), 0.85 (t, 6H).

5-[E-4-(N,N-Diethylamino)phenylene]-5'-bromo-3,3'-
10 dihexyl-2,2'-bithiophene. To a solution of 5-(5'-bromo-3,3'-dihexyl-2,2'-bithienyl)methylphosphonate (7.5 g, 13.3 mmol) and potassium t-butoxide (1.7 g, 14.6 mmol) in 100 ml of THF was added 4-(diethylamino)benzaldehyde (2.4 g, 13.3 mmol) in 20 ml of THF at 0 °C during 30 min. This is
15 stirred for 4 h and normal workup gave a yellow viscous oil (7.0 g, 90 %). ¹H-NMR (CDCl₃, ppm): δ 7.32 (d, 2H, J=5 Hz), 6.90 (d, 1H, J=7.5 Hz), 6.85 (s, 1H), 6.80 (s, 1H), 6.78 (d, 1H, J= 7.5 Hz), 6.67 (d, 2H, J=5 Hz), 3.41 (q, 4H), 2.50 (t, 2H), 2.41 (t, 2H), 1.50 (m, 4H), 1.21 (m,
20 12H), 1.17 (t, 6H), 0.87 (t, 6H).

5-[E-4-(N,N-Diethylamino)phenylene]-5'-formyl-3,3'-
dihexyl-2,2'-bithiophene. n-Butyllithium (12 ml, 2.5 M in hexanes, 30 mmol) was added dropwise to a solution of 5-[E-4-(N,N-diethylamino)phenylene]-5'-bromo-3,3'-dihexyl-
25 2,2'-bithiophene (7 g, 12 mmol) in 80 ml of THF over 15 min at -78 °C. Then the reaction mixture was allowed to gradually rise to -20 °C and 5 ml of anhydrous DMF was added. After the mixture was stirred for 3 h, 50 ml of 1N HCl was added dropwise to terminate the reaction. The
30 normal workup was then carried out and the crude product was purified by column chromatography over silica gel, eluting with ethyl acetate/hexane (1:5) to afford a yellow viscous oil (5.7 g, 89 %). ¹H-NMR (CDCl₃, ppm): δ 9.85 (s,

1H), 7.64 (s, 1H), 7.31 (d, 2H, $J=5$ Hz), 6.96 (d, 1H, $J=7.5$ Hz), 6.90 (s, 1H), 6.79 (d, 1H, $J=7.5$ Hz), 6.50 (d, 2H, $J=5$ Hz), 3.36 (q, 4H), 2.61 (t, 2H), 2.50 (t, 2H), 1.55 (m, 4H), 1.26 (m, 12H), 1.17 (t, 6H), 0.85 (t, 6H).

5 2-Dicyanomethylen-3-cyano-4-{5-[E-(4-N,N-diethylamino)-phenylene-3,3'-dihexyl-2,2'-bithien-5']-E-vinyl}-5,5-dimethyl-2,5-dihydrofuran (Chromophore). To a solution of sodium ethoxide (0.8 ml, 21 wt% solution in ethanol) in 100 ml of ethanol was added 5-[E-4-(N,N-
10 diethylamino)phenylene]-5'-formyl-3,3'-dihexyl-2,2'-bithiophene (5.7 g, 10.6 mmol) and 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (2.6 g, 13.1 mmol).

The reaction mixture was stirred and refluxed for 6 h. When TLC indicated that the reaction was almost complete,
15 the mixture was cautiously poured into water and kept at 0 °C overnight. The crystalline precipitate was recrystallized from ethanol to give shiny crystals of the chromophore (5.5 g, 72 %). $^1\text{H-NMR}$ (CDCl_3 , ppm): δ 7.80 (d, 2H, $J=12.5$ Hz), 7.40 (s, 1H), 7.34 (d, 1H, $J=8$ Hz), 6.95
20 (d, 1H, $J=12.5$ Hz), 6.88 (s, 1H), 6.82 (d, 1H, $J=12.5$ Hz), 6.65 (d, 1H, $J=8$ Hz), 6.53 (d, 2H, $J=12.5$ Hz), 3.38 (q, 4H), 2.62 (t, 2H), 2.55 (t, 2H), 1.76 (s, 6H), 1.57 (m, 4H), 1.27 (m, 12H), 1.18 (t, 6H), 0.87 (t, 6H).

25 Referring to FIG. 10, a representative bridge modification by bithiophene insertion and dimethyldioxine ring modification is illustrated. The resulting chromophore has an much improved r_{33} of 95 pm/V at 1.06 μm .

Several exemplary preferred ring-locked tricyano
30 electron acceptor groups are illustrated in FIG. 11. In FIG. 11, R_1 to R_9 = H, $-\text{C}_n\text{H}_{2n+1}$, $n = 1-30$ including primary, secondary, tertiary and any branched alkyl groups, or any alkyl group with 1-30 carbon atoms functionalized with one

or more of the following functional groups: hydroxy, ether, ester, amino, silyl, siloxy.

The five-membered-ring-locked tricyano acceptor (cyanofuran acceptor, TCF in FIG. 11) has been modified to
5 further increase electro-optic activity and chromophore stability. According the present invention, a large number of atoms and organic groups (e.g., carbonyl) have been used in place of the furan oxygen in the electron acceptor group leading to improved electrooptic and
10 optical properties. Six-membered-ring-locked analogs (TCP) have also been developed. The oxygen atom of the furan ring and the pyran ring (in TCF and TCP) is replaced by a methylene moiety to produce the desired effect of blue shifting the optical absorption spectrum leading to
15 lower optical loss for some electrooptic applications.

Referring to FIG. 12, a modified version of CLD is shown where the cyanofuran acceptor has been modified by replacement of the furan ring with an isophorone ring structure. This has the desired effect of blue shifting
20 the optical absorption spectrum leading to lower optical loss for some electrooptic applications.

Synthesis of Chromophore With Isophorone Structure in Electron Acceptor Group

25 To a mixture of isophorone (400g), EtOH (1000ml), NaOH (20g) and water (30ml) was added 1.2eq, 3.473mol, 394.76g of 30% H₂O₂ in portions at RT. After 4 hour of stirring, the mixture was neutralized with dilute acetic acid and extracted with diethyl ether. The extract was
30 dried over MgSO₄, condensed via rotary evaporation. The crude product was used in the next reaction without purification.

To a solution of the above crude product in 500ml EtOH was added a solution of 2.89mol, 108g KCN/ 150g water in portions over 0.5 h. The mixture was refluxed for 1 h. Rotovap at 60 °C to remove EtOH. The residue was
5 neutralized with 6N hydrochloric acid. The product was collected by filtration. The crude product was purified with column chromatography using 4/1 hexanes/EtOAc as eluent to give 180g pure product.

TCI (2-cyano-3-dicyanomethylene-1,5,5-
10 dimethylcyclohexene): A mixture of 2-cyanoisophorone(14.19g, 86.9mmol), malononitrile (6.89g), EtOH (15ml) and EtONa (100mmol, 6.88g) was heated in 80-90C bath for 1h. The mixture was poured water, neutralized with acetic acid and extracted with ethyl
15 acetate. The extract was condensed and purified with silica gel column chromatography. Recrystallization of the product from EtOAc/hexane gave gray crystals with mp of 103.5-105.5. Elemental analysis: calcd. C 73.91, H 6.20, N 19.89; found C 73.93, H 6.26, N 19.97.

20 The chromophore (CLD-54) was synthesized in a manner similar to the synthesis of chromophore CLD-1 in FIG. 2. UV-vis absorption: 600 nm in dioxane, 663 nm in chloroform.

Referring to FIG. 13, alternative donor structures
25 for the FTC, CLD, GLD and ZLD chromophores are illustrated. It has been observed that chromophores of the FTC, CLD, GLD and ZLD type have been systematically improved by the utilization of the new donor structures which provide improved electrooptic activity as the result
30 of an improved inductive (electron donating) effect and through better overlap of π -electron orbitals due to steric and resonance effects. Exemplary FTC chromophore structures with modified donor structures are illustrated

in FIGs. 14A and 14B. All of these structures have been incorporated into a variety of polymer lattices. In FIG. 13, R_1 to $R_2 = H, -C_nH_{2n+1}$, $n = 1-30$ including primary, secondary, tertiary and any branched alkyl groups, or any
5 alkyl group with 1-30 carbon atoms functionalized with one or more of the following functional groups: hydroxy, ether, ester, amino, silyl, siloxy.

Preparation of a Polyester Containing CLD-5 Chromophore

10 All chromophores functionalized with reactive groups have been incorporated into a variety of polymer lattices by reacting them with various polymerization and polymerization coupling reagents. Such structures exhibit excellent thermal stability (i.e., no loss of electrooptic
15 activity to greater than 100°C). The preparation of a polyester containing CLD-5 chromophore is illustrated in FIG. 15 and discussed below.

Preparation of 19.6wt% CLD-5 loaded polyester. In dry box, a mixture of 0.4mmol of terephthaloyl dichloride,
20 0.0838 mmol CLD-5, 2ml THF and 0.1mmol of triethylamine was stirred at 30 °C for 10h. Then 0.366mmol of isopropylidenediphenol and 0.69 mmol of triethylamine were added. Stirring was continued for 26h later and the mixture was precipitated from MeOH. The polymer was
25 dissolved in methylene chloride and reprecipitated by dropping the solution into methanol. The product was collected by filtration and dried in vacuo.

Continued improvement in theoretical tools used to
30 guide the design of improved electrooptic materials has also been made. Monte Carlo Molecular Dynamical Methods as well as equilibrium statistical mechanical methods have been developed to guide the design of improved materials.

As shown in FIG. 16, these various methods give comparable results. More specifically, a comparison of equilibrium and molecular dynamical (Monte Carlo) calculations is provided. The solid lines are the equilibrium statistical
5 mechanical results while the Monte Carlo results are given by connected dots. The variation of electrooptic activity (divided by molecular polarizability) versus chromophore concentration in the polymer lattice is given for two
10 values of the electric poling field. For the lower field value, the Monte Carlo results are displaced downward to make comparison of the functional dependence more easily visualized.

The organic chromophores of the present invention exhibit exceptional molecular optical nonlinearity,
15 thermal stability, and low optical absorption at telecommunication wavelengths. The chromophore materials of the present invention are suitable for processing into hardened polymers for electrooptic devices employing
20 protocols previously developed for other chromophores. The materials are fully amenable to all processing steps necessary for the fabrication of such devices.

According to the present invention, these materials can be employed not only in conventional electrooptic modulator device configurations but also in devices
25 employing a constant bias field which permits the full potential of the materials to be demonstrated. Referring to FIG. 17, an exemplary preferred electrooptic device 1700 employing a constant electric field bias is
30 illustrated. The illustrated electrooptic device 1700 includes a modulator chip 1702, a fiber 1704, a thermoelectric cooler 1706, a temperature controller 1708, a thermister 1710, and a bias tee 1712 (including a

resistor and a capacitor) configured as shown providing a light output indicated by arrow 1714.

Referring to FIG. 18, an exemplary preferred Mach Zehnder modulator 1800 incorporating a chromophore material of the present invention is illustrated. The illustrated modulator 1800 includes a Si substrate 1802, an Epoxylite (3 μm) layer 1804, a PU-chromophore (1.5 μm) layer 1806, a NOA73 (3.5 μm) layer 1808, a waveguide 1810 and an electrode 1812 configured as shown with light indicated by arrows 1814, 1816.

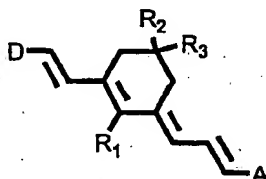
Referring to FIG. 19, the materials of the present invention are shown in the form of microstrip lines in an exemplary preferred microwave phase shifter 1900 of the type employed in optically controlled phase array radars. The illustrated microwave phase shifter 1900 includes microstrip lines 1902, 1904, a DC control electrode 1906, a DC source 1908, a photodetector 1910 and an optical waveguide 1912 configured as shown with light indicated by arrow 1914.

Those skilled in the art will appreciate that various adaptations and modifications of the just described preferred embodiment can be configured without departing from the scope and spirit of the invention. Therefore, it is to be understood that, within the scope of the appended claims, the invention may be practiced other than as specifically described herein.

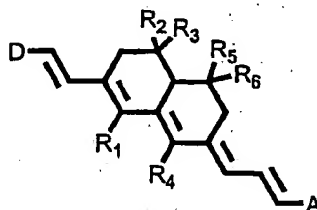
WE CLAIM:

1. A nonlinear optical device comprising:
an active element including a chromophore formed as:

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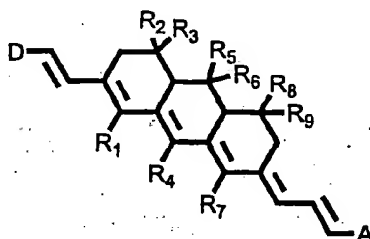


10



, or

15



20

wherein D is an electron donor group;

wherein A is an electron acceptor group;

wherein R_1 to R_9 = H, $-C_nH_{2n+1}$, n = 1-30 including primary, secondary, tertiary and any branched alkyl groups, or any alkyl group with 1-30 carbon atoms functionalized with one or more of the following functional groups: hydroxy, ether, ester, amino, silyl, siloxy.

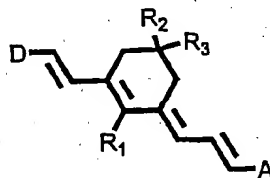
1 2. A nonlinear optical device comprising:
2 an active element formed from a chromophore including
3 an electron donor group,
4 an electron acceptor group, and
5 a bridge structure between the electron donor
6 group and the electron acceptor group;
7 wherein the electron acceptor group is connected to
8 the bridge structure with a conjugated diene.

1 3. The nonlinear optical device of claim 2 wherein
2 the bridge structure includes at least one side group.

1 4. The nonlinear optical device of claim 2 wherein
2 the bridge structure includes an alicyclic ring.

1 5. The nonlinear optical device of claim 2 wherein
2 the chromophore is formed in a polymer matrix.

1 6. A nonlinear optical device comprising:
2 an active element formed from a chromophore including
3 an electron donor group (D),
4 an electron acceptor group (A), and
5 a ring-locked bridge structure between the
6 electron donor group and the electron acceptor group;
7 wherein the ring-locked bridge structure is formed as

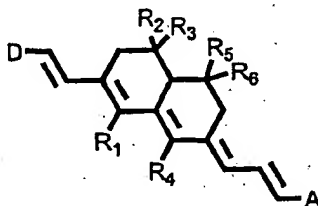


12
13 wherein R_1 to $R_3 = H$, $-C_nH_{2n+1}$, $n = 1-30$ including
14 primary, secondary, tertiary and any branched alkyl

15 groups, or any alkyl group with 1-30 carbon atoms
 16 functionalized with one or more of the following
 17 functional groups: hydroxy, ether, ester, amino, silyl,
 18 siloxy.

1 7. The nonlinear optical device of claim 6 wherein
 2 the chromophore is formed in a polymer matrix.

1 8. A nonlinear optical device comprising:
 2 an active element formed from a chromophore including
 3 an electron donor group (D),
 4 an electron acceptor group (A), and
 5 a ring-locked bridge structure between the
 6 electron donor group and the electron acceptor group;
 7 wherein the ring-locked bridge structure is formed as

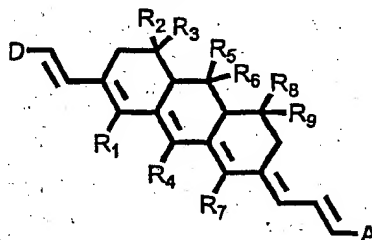


14 wherein R_1 to $R_6 = H$, $-C_nH_{2n+1}$, $n = 1-30$ including
 15 primary, secondary, tertiary and any branched alkyl
 16 groups, or any alkyl group with 1-30 carbon atoms
 17 functionalized with one or more of the following
 18 functional groups: hydroxy, ether, ester, amino, silyl,
 19 siloxy.

1 9. The nonlinear optical device of claim 8 wherein
 2 the chromophore is formed in a polymer matrix.

1 10. A nonlinear optical device comprising:
 2 an active element formed from a chromophore including

3 an electron donor group (D),
 4 an electron acceptor group (A), and
 5 a ring-locked bridge structure between the
 6 electron donor group and the electron acceptor group;
 7 wherein the ring-locked bridge structure is formed as



14 wherein R_1 to R_9 = H, $-C_nH_{2n+1}$, n = 1-30 including
 15 primary, secondary, tertiary and any branched alkyl
 16 groups, or any alkyl group with 1-30 carbon atoms
 17 functionalized with one or more of the following
 18 functional groups: hydroxy, ether, ester, amino, silyl,
 19 siloxy.

1 11. The nonlinear optical device of claim 10 wherein
 2 the chromophore is formed in a polymer matrix.

1 12. A nonlinear optical device comprising:
 2 an active element formed from a chromophore including
 3 an electron donor group,
 4 a ring-locked tricyano electron acceptor group,
 5 and
 6 a bridge structure between the electron donor
 7 group and the ring-locked tricyano electron acceptor group.

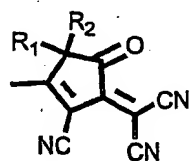
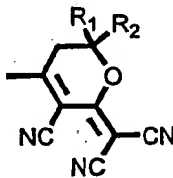
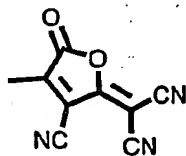
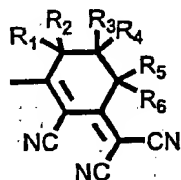
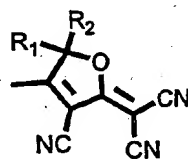
1 13. The nonlinear optical device of claim 12 wherein
 2 the ring-locked tricyano electron acceptor group is
 3 connected to the bridge structure with a conjugated diene.

1 14. The nonlinear optical device of claim 12 wherein
2 the ring-locked tricyano electron acceptor group comprises
3 an isophorone structure.

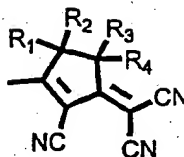
1 15. The nonlinear optical device of claim 12 wherein
2 the bridge structure comprises a fused ring system.

1 16. The nonlinear optical device of claim 12 wherein
2 the chromophore is formed in a polymer matrix.

1 17. The nonlinear optical device of claim 12 wherein
2 the ring-locked tricyano electron acceptor group comprises:



, or



1 18. A nonlinear optical device comprising:
 2 an active element formed from a chromophore including
 3 an electron donor group,
 4 an electron acceptor group, and
 5 a bridge structure between the electron donor
 6 group and the electron acceptor group, the bridge structure
 7 including a bithiophene unit.

1 19. The nonlinear optical device of claim 18 wherein
 2 the bridge structure further includes a modified isophorone
 3 unit.

1 20. The nonlinear optical device of claim 18 wherein
 2 the electron acceptor group comprises a tricyano electron
 3 acceptor group.

1 21. The nonlinear optical device of claim 18 wherein
 2 the chromophore is formed in a polymer matrix.

1 22. A nonlinear optical device comprising:
 2 an active element formed from a chromophore including
 3 an electron donor group,
 4 an electron acceptor group, and
 5 a bridge structure between the electron donor
 6 group and the electron acceptor group;
 7 wherein the electron donor group is formed as
 8

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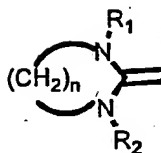
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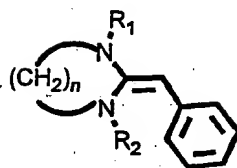
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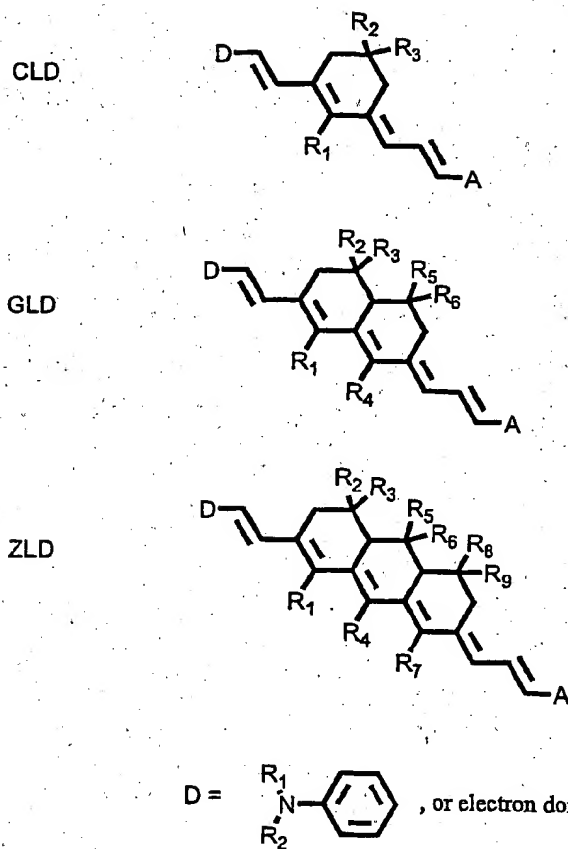
19 wherein R_1 to R_2 = H, $-C_nH_{2n+1}$, n = 1-30 including
20 primary, secondary, tertiary and any branched alkyl
21 groups, or any alkyl group with 1-30 carbon atoms
22 functionalized with one or more of the following
23 functional groups: hydroxy, ether, ester, amino, silyl,
24 siloxy.



, or



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A = any of the acceptors shown in Figure 11.

FIG. 1

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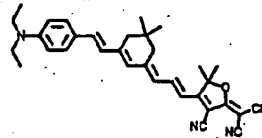
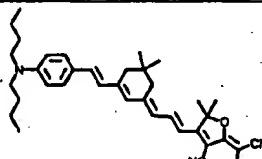
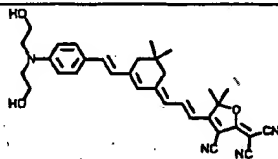
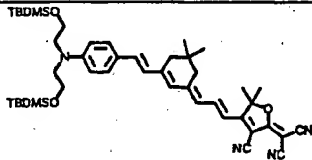
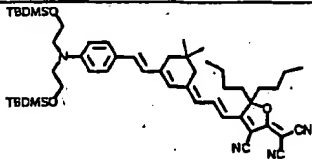
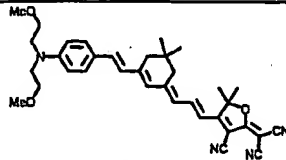
Chromophores	λ_{max} in dioxane (nm)	λ_{max} in chloroform (nm)
 CLD-72	640	705
 CLD-7	646	715
 CLD-2	629.8	662.6
 CLD-1	632.4	692.2
 CLD-8	637	689
 CLD-6	631	676

FIG. 2

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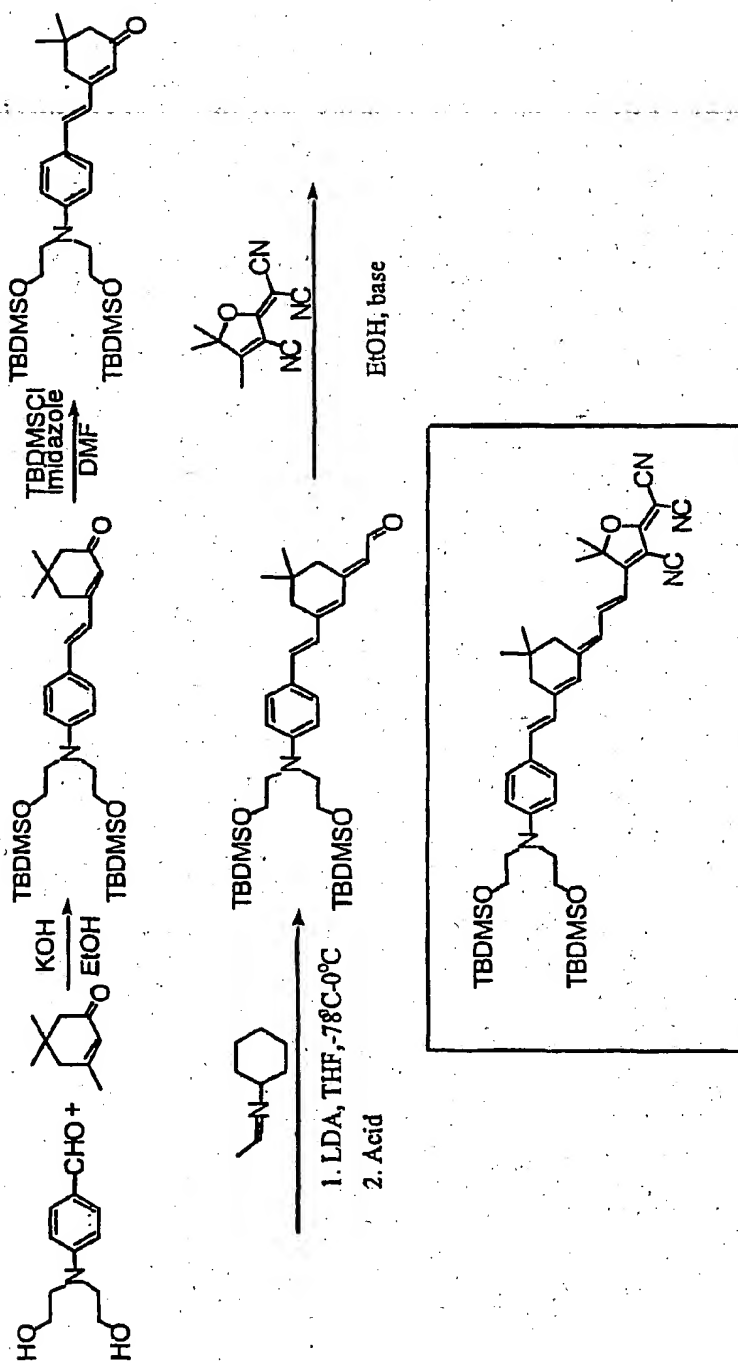


FIG. 3

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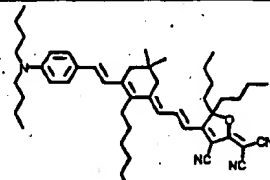
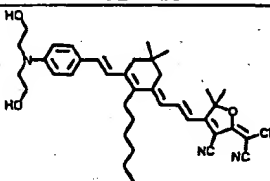
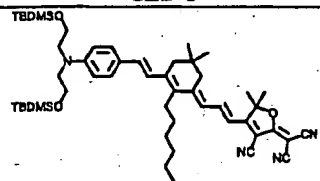
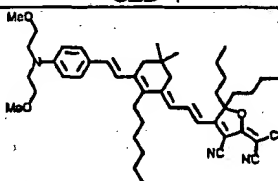
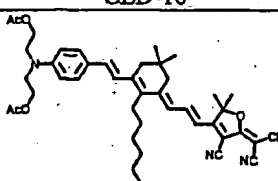
Chromophores	λ_{max} in dioxane (nm)	λ_{max} in chloroform (nm)
 CLD-11	648	709
 CLD-5	628.4	660.8
 CLD-4	633.8	689.2
 CLD-10	633	672
 CLD-9	613	653

FIG. 4

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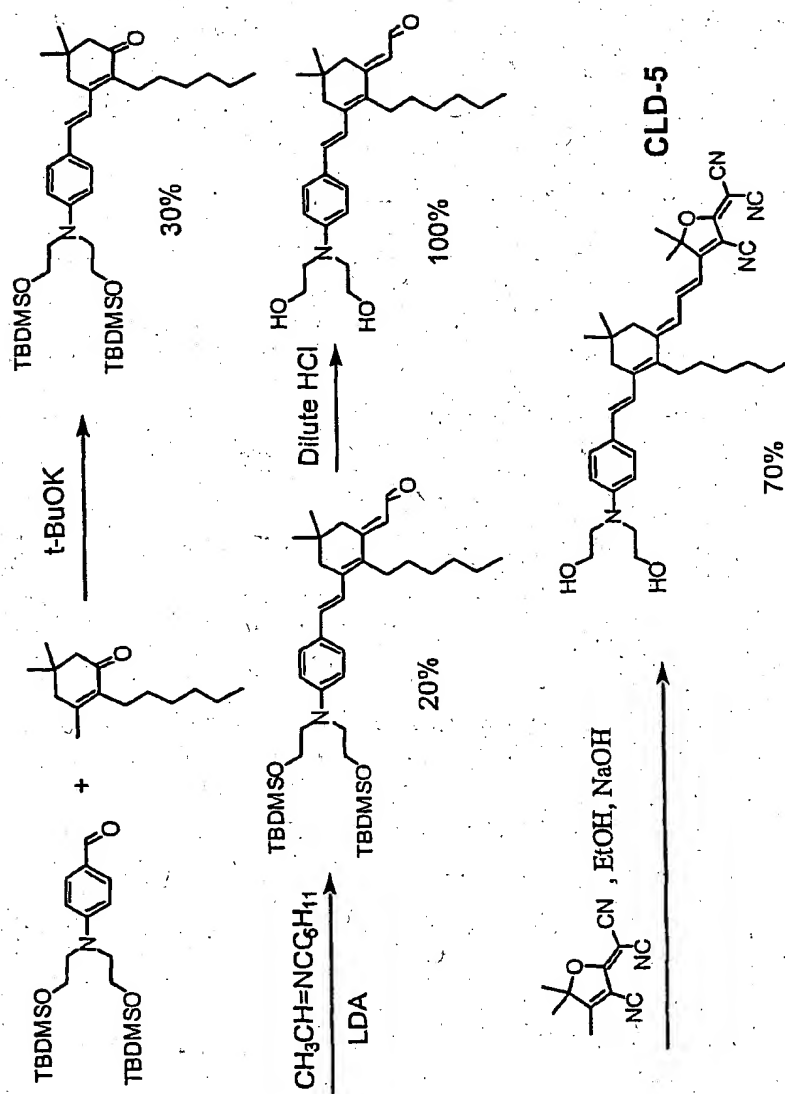


FIG. 5

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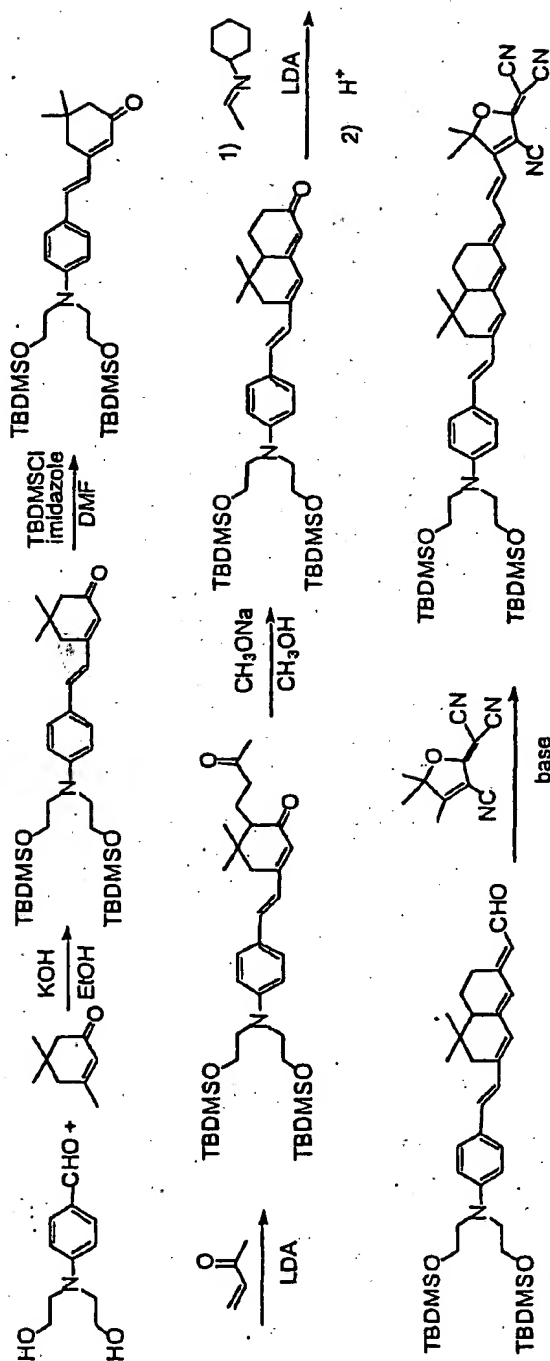


FIG. 6

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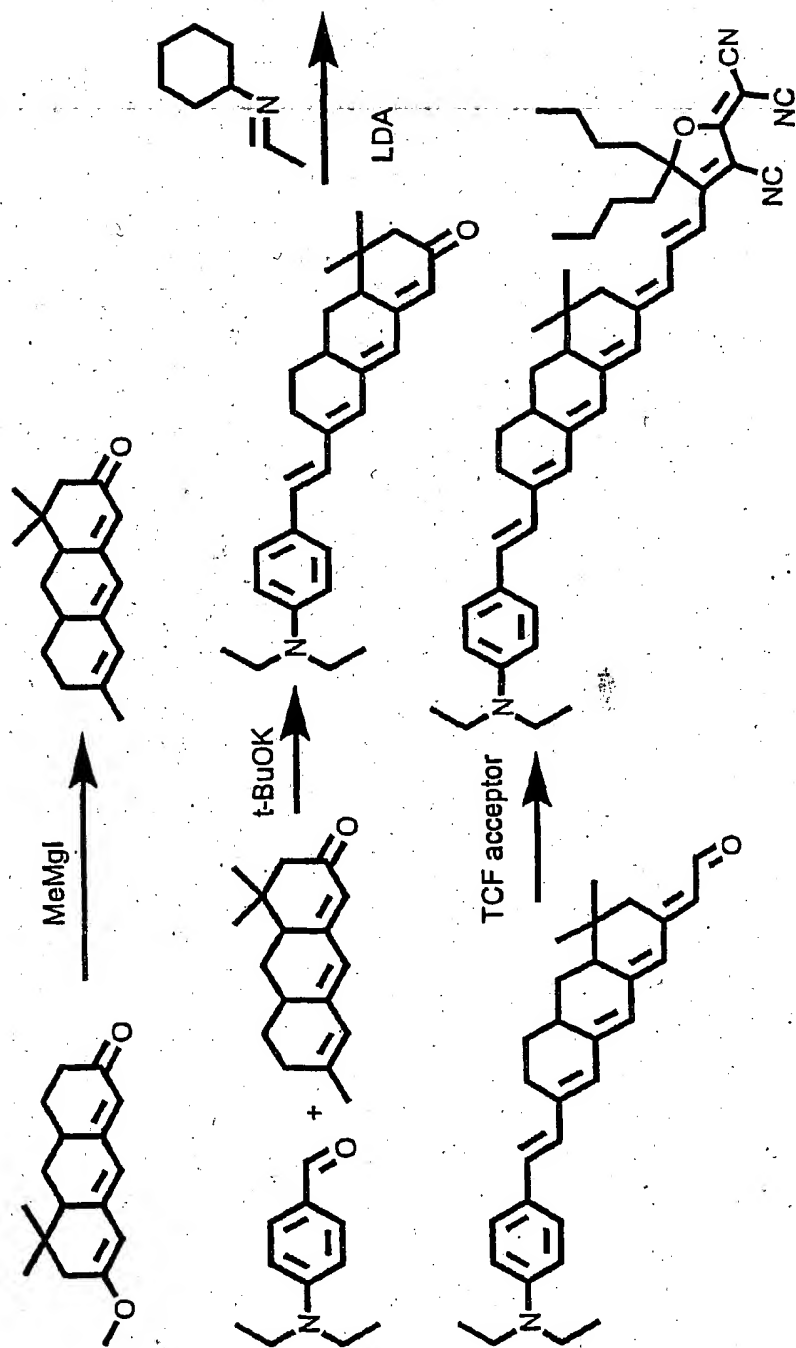


FIG. 7

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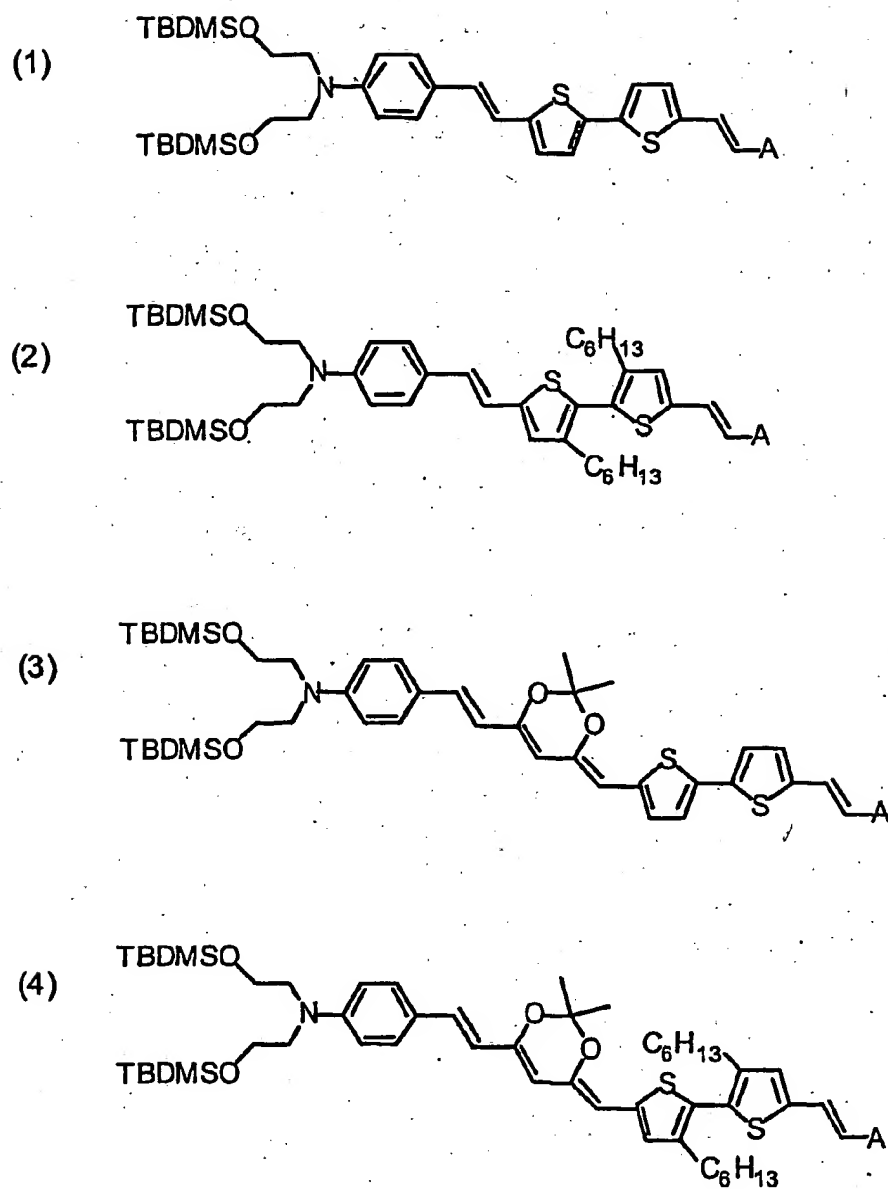
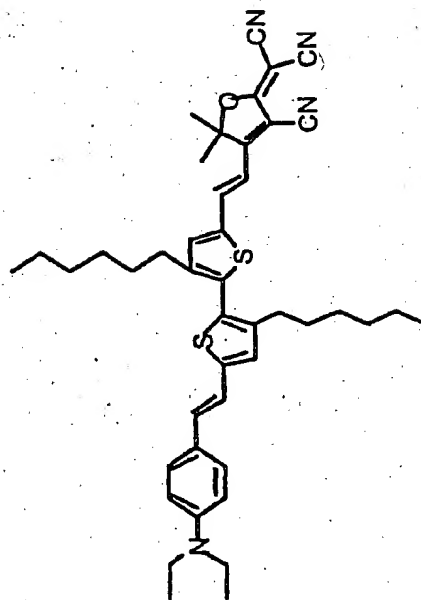


FIG. 8

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Synthesis, thermal and optical properties

M.W.: 717.06 for $C_{44}H_{52}N_4OS_2$

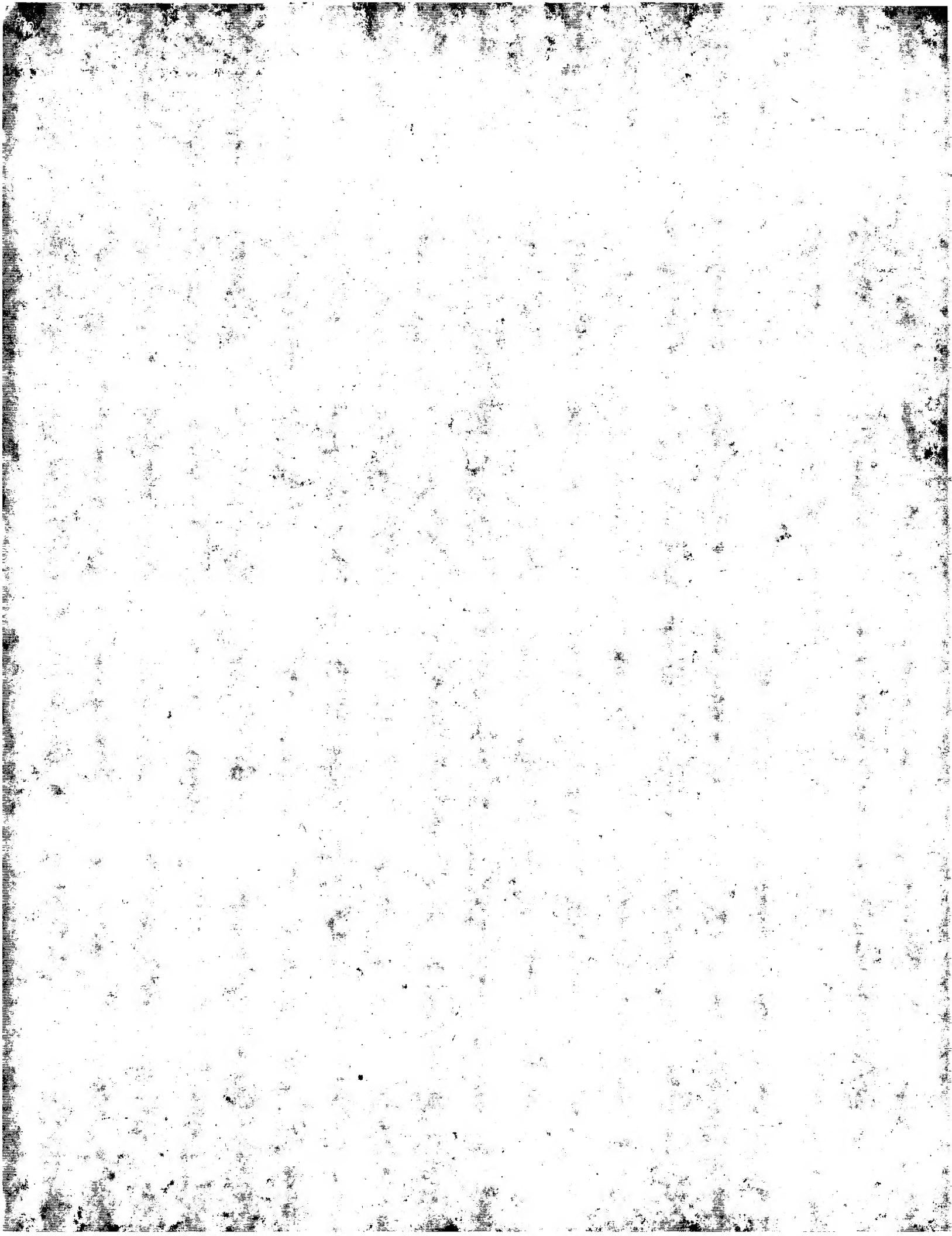
M.P: 187 °C

Td: 412 °C (by TGA, 4°C/min)

UV-vis: 608 nm in chloroform

556 nm in dioxane

FIG. 9A



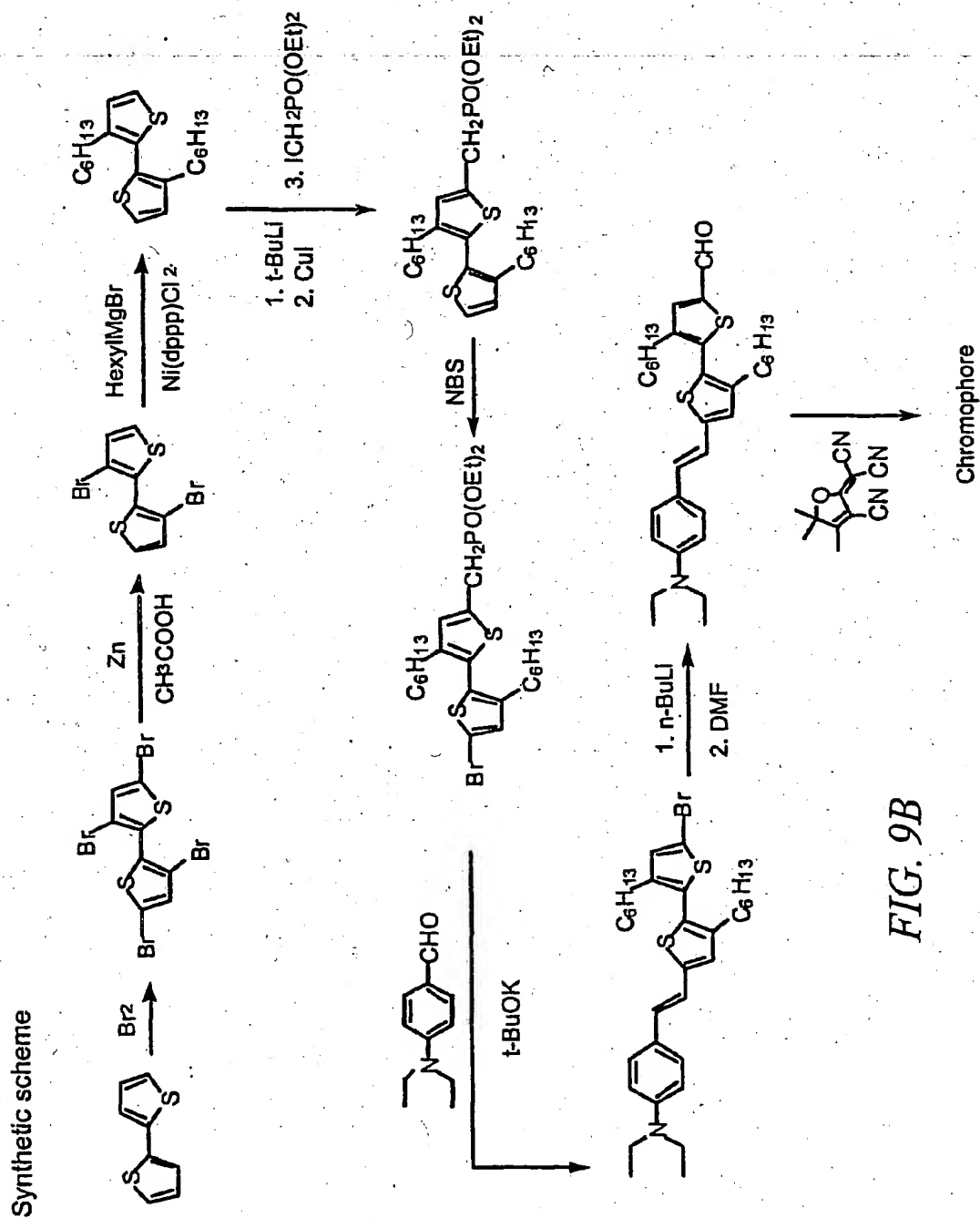


FIG. 9B

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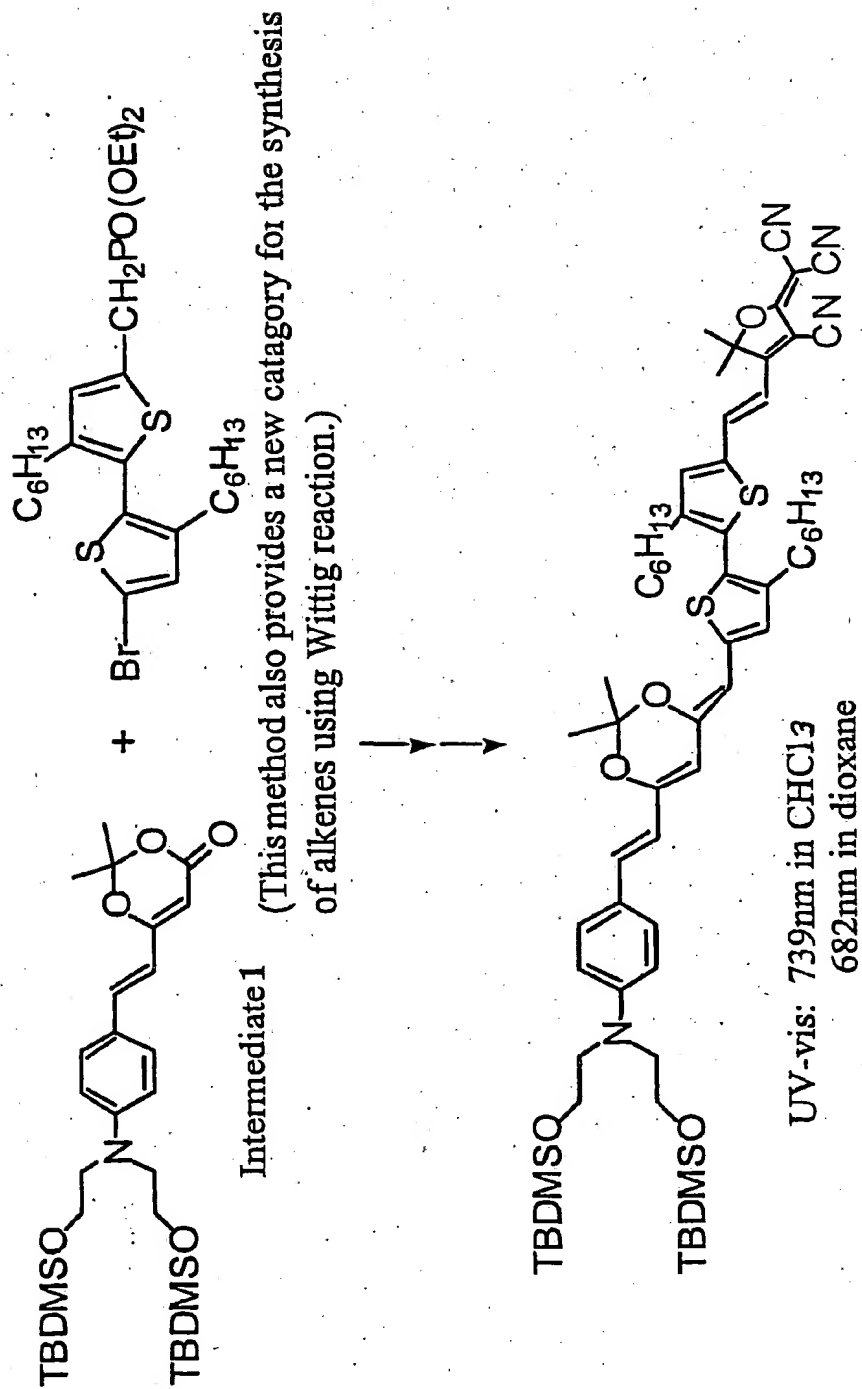
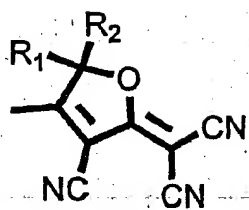
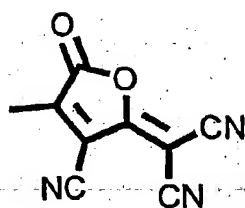


FIG. 10

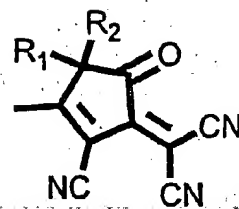
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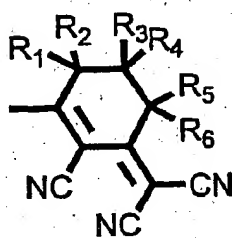
TCF



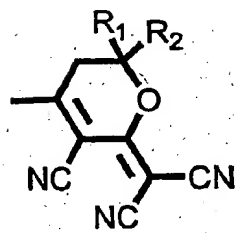
TCFO



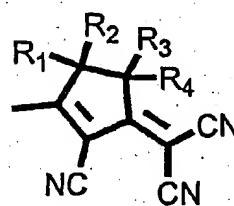
TCCPO



TCI



TCP



TCCP

FIG. 11

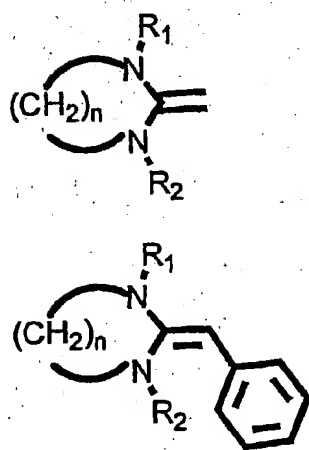


FIG. 13

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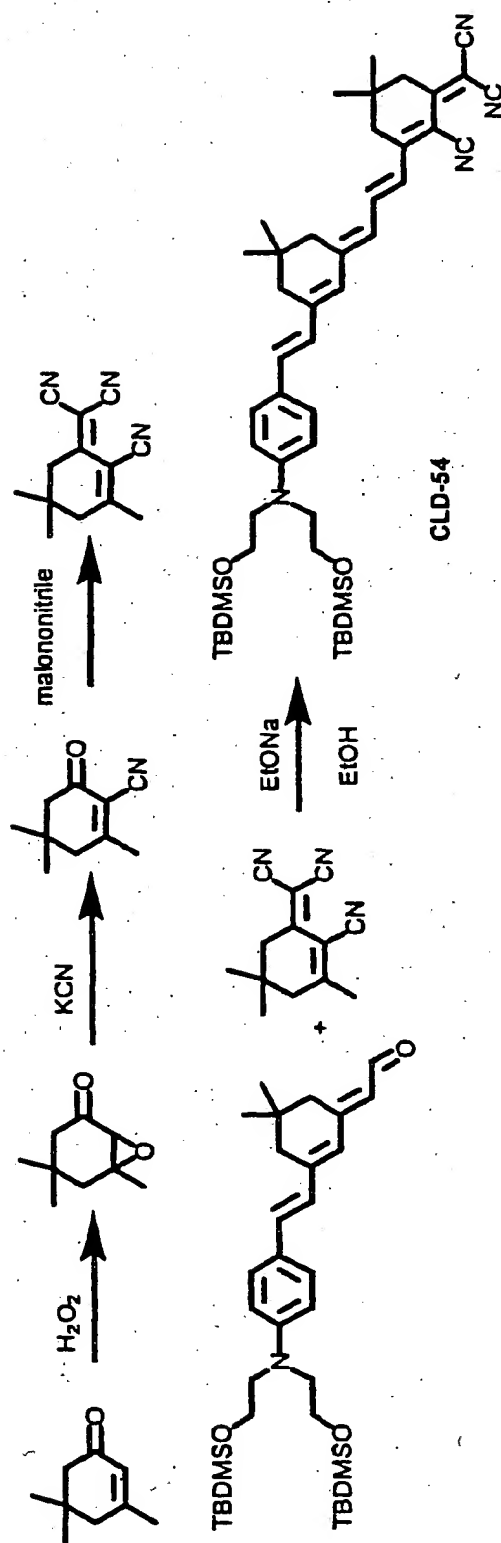


FIG. 12

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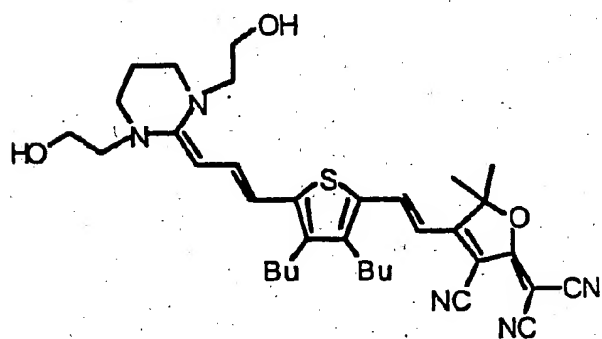
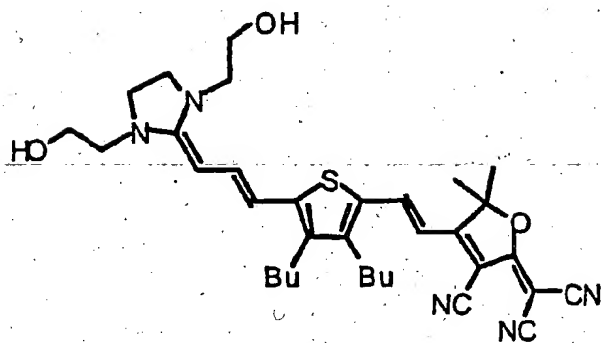
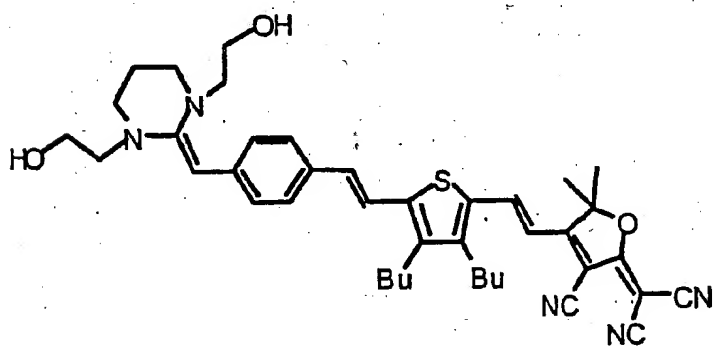
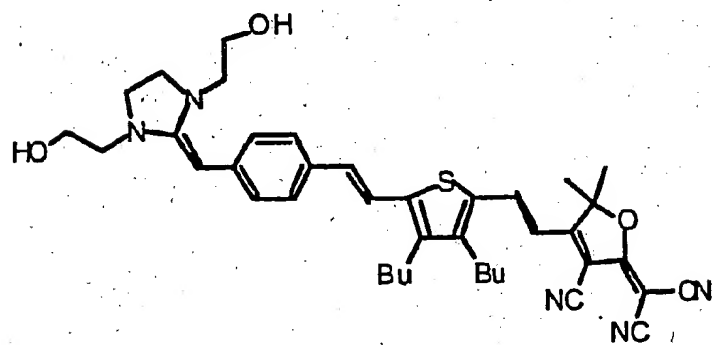
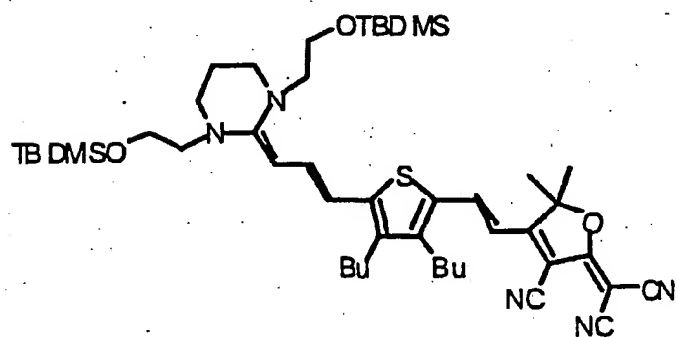
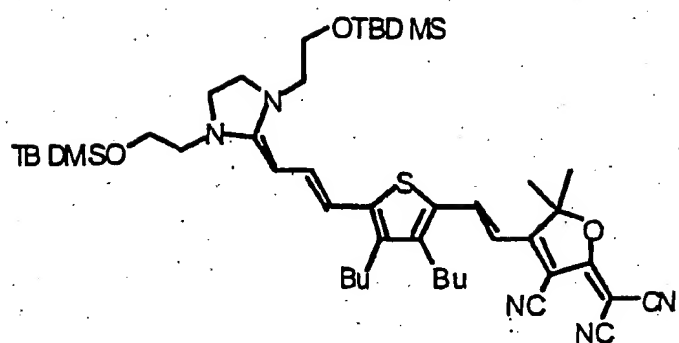
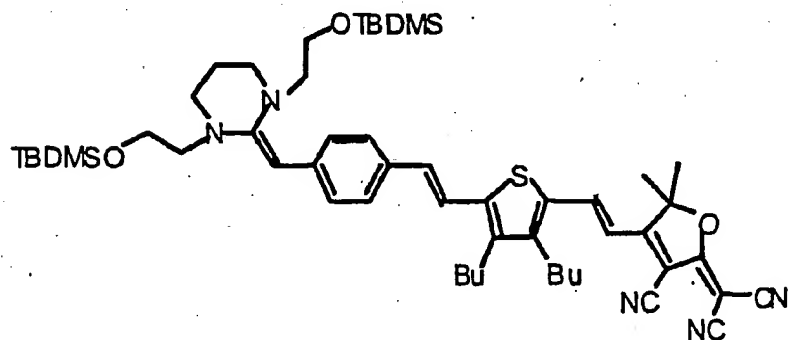
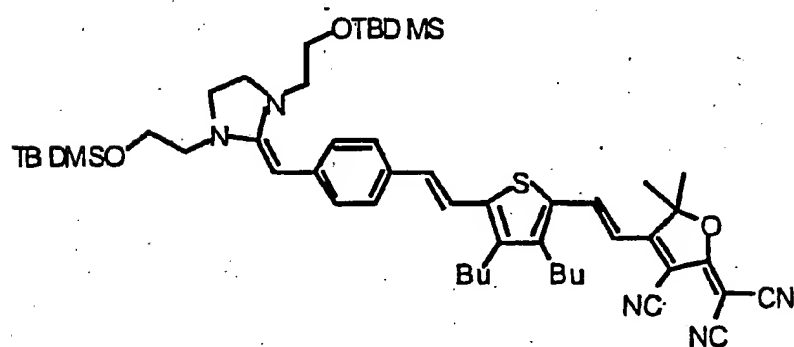


FIG. 14A



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*FIG. 14B*

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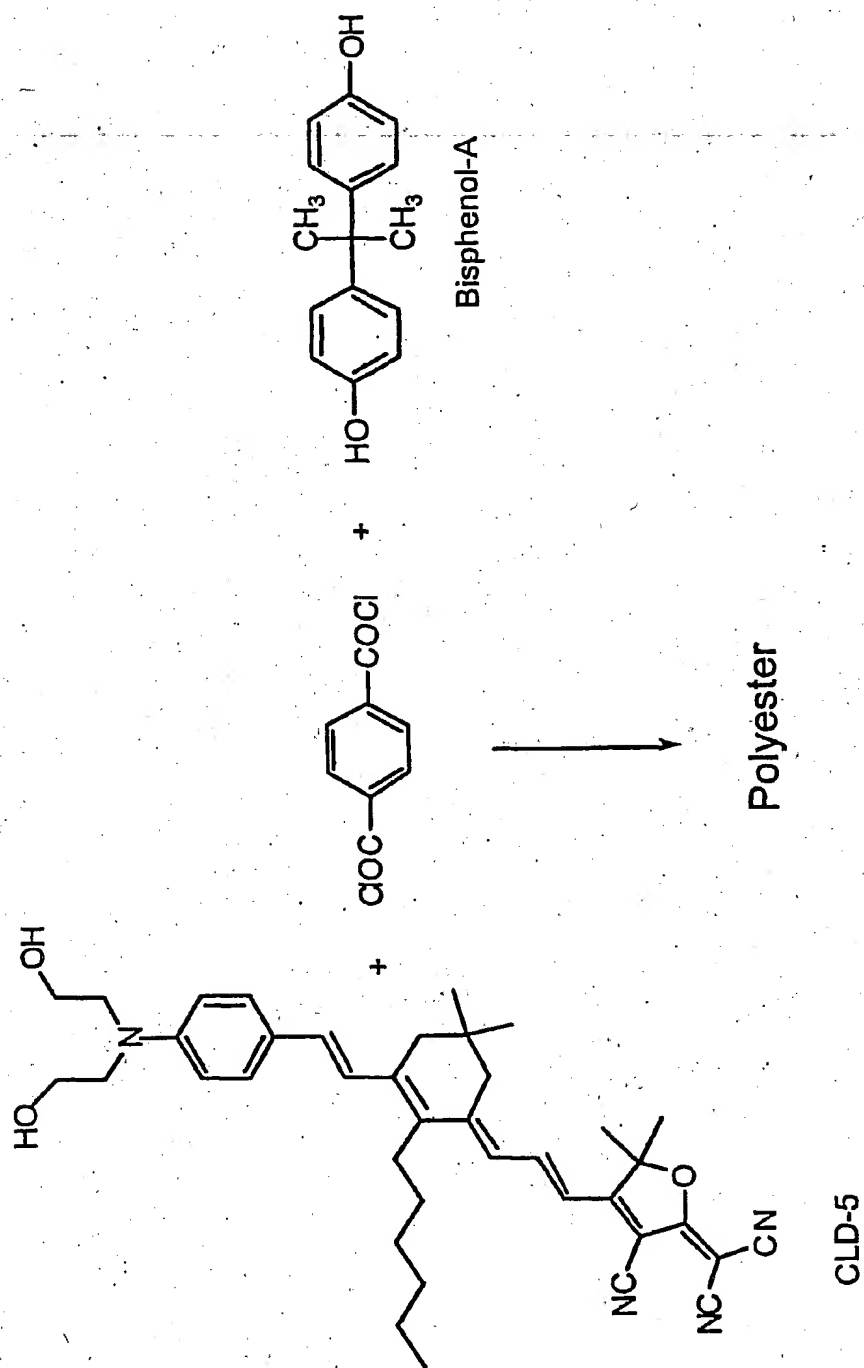
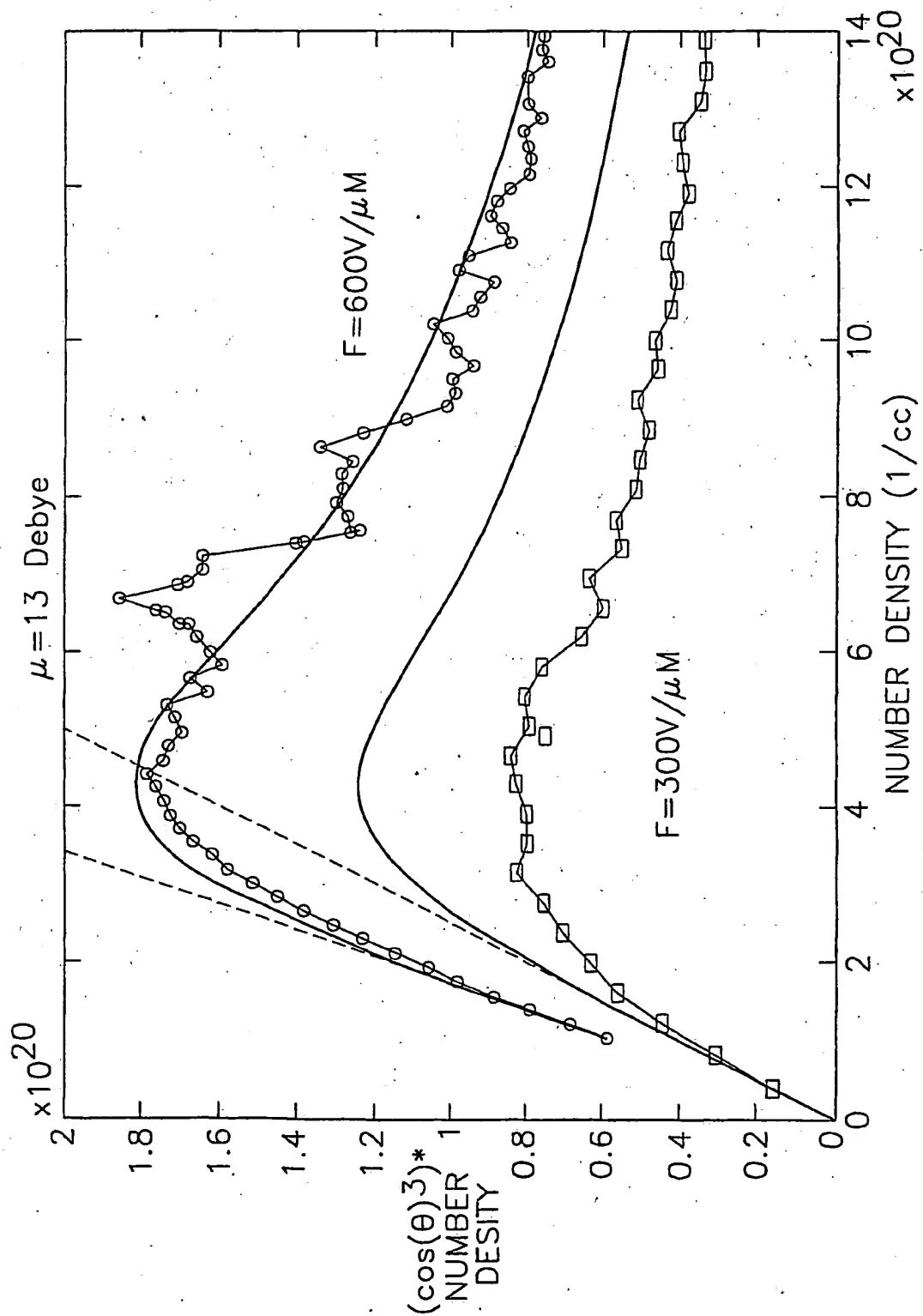


FIG. 15

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FIG. 16



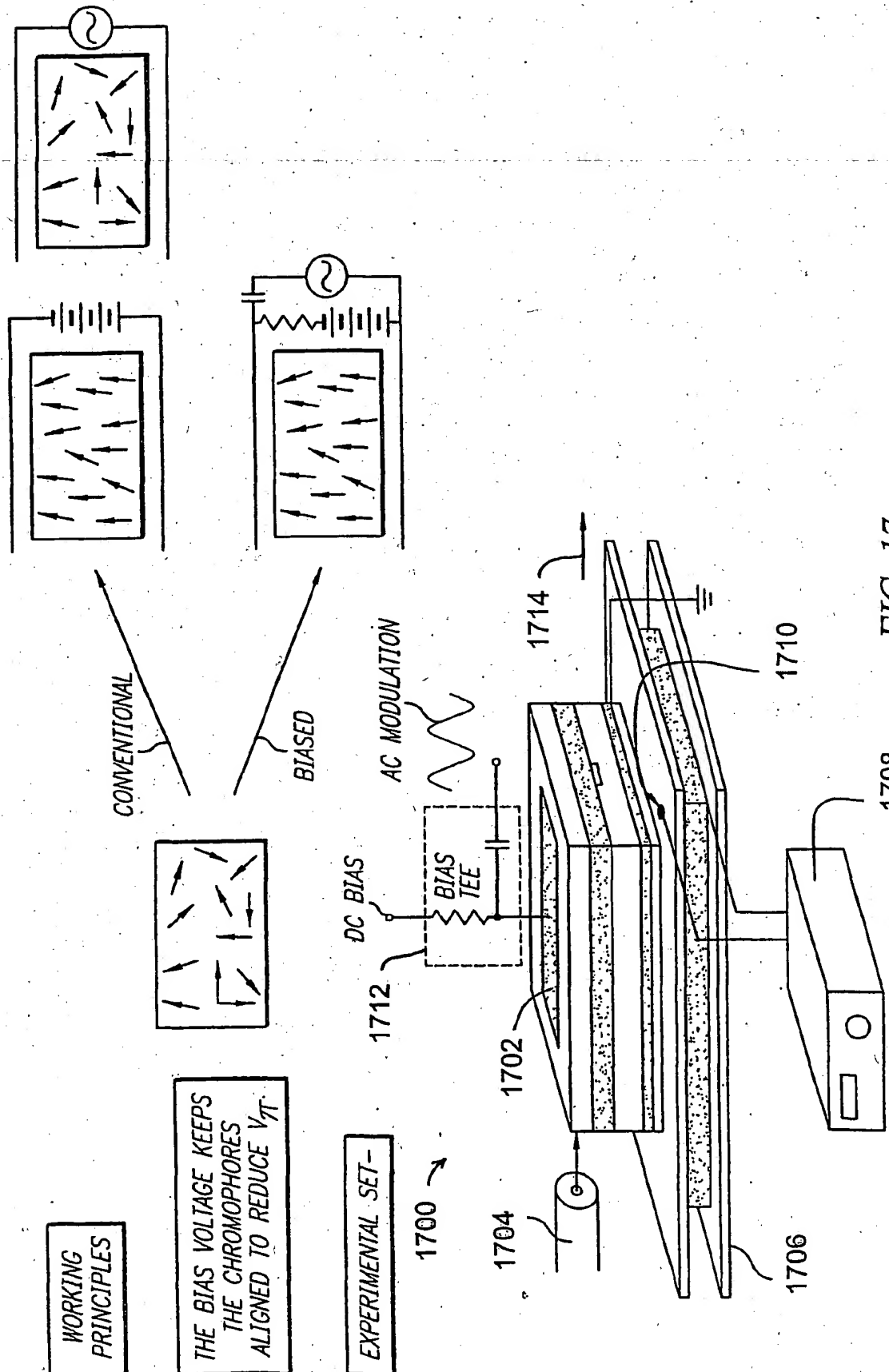


FIG. 17

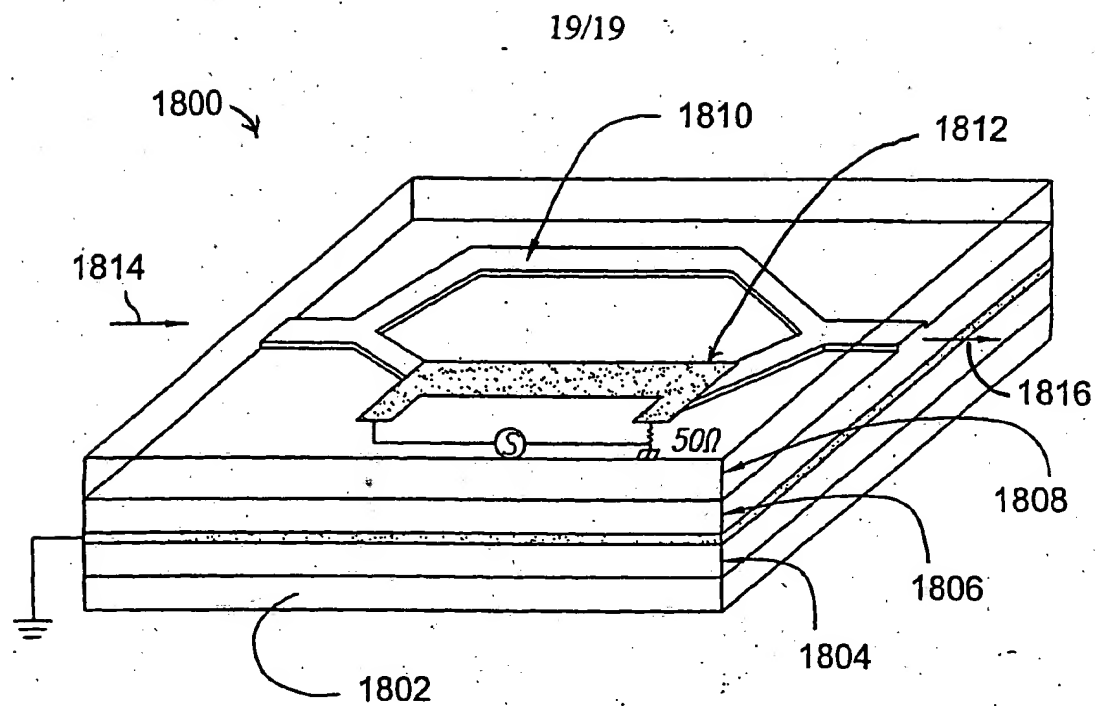


FIG. 18

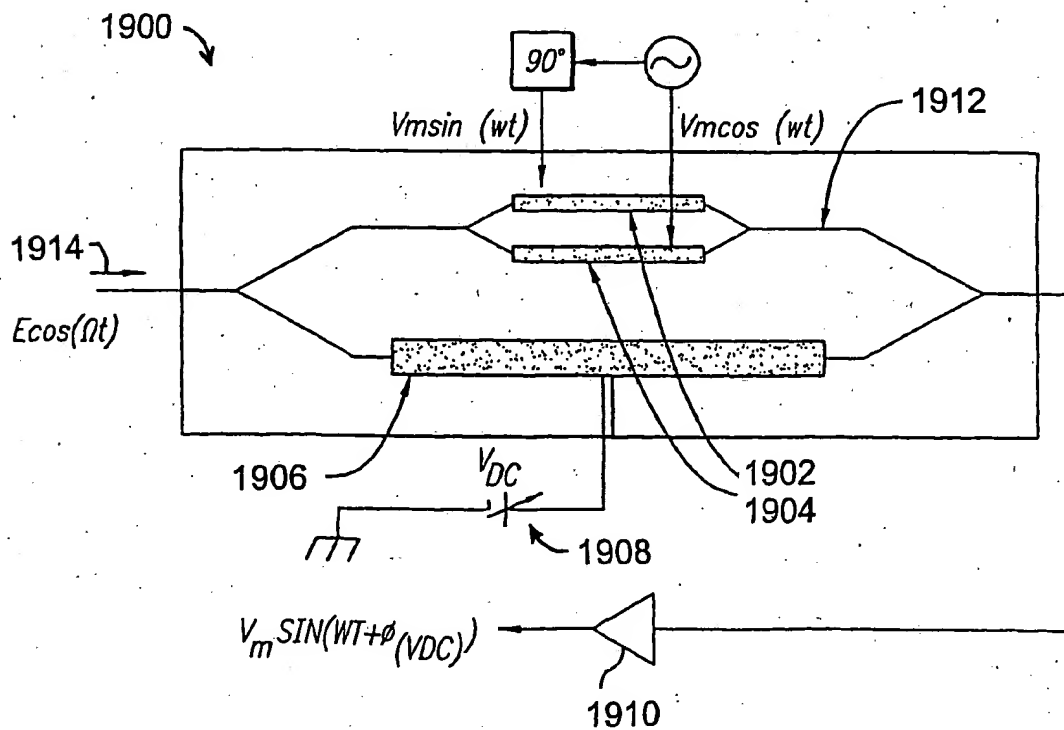


FIG. 19

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/01655

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : F21V 9/00, G02F 1/35

US CL : 252/582, 587; 359/328

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/582, 587; 359/328

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST, CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,432,286 A (CABRERA et al.) 11 July 1995, see examples.	18, 21
X	US 5,514,799 A (VARANASI et al.) 07 May 1996, see example 14	18, 20, 21
X	US 5,676,884 A (TIERS et al.) 14 October 1997, see Table I.	2, 5, 5
X	US 5,804,101 A (MARDER et al.) 08 September 1998, see claim 1 and examples.	2, 3, 5
X	US 5,738,806 A (BECKMANN et al.) 14 April 1998, see examples.	18, 21
X	US 5,679,763 A (JEN et al.) 21 October 1997, see example 2 and claim 21.	2, 5, 22

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 MARCH 2001

Date of mailing of the international search report

26 APR 2001

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Facsimile No. (703) 305-3230

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PHILIP C. TUCKER

Telephone No. (703) 308-0651

 Jean Proctor 
 Paralegal Specialist

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/01655

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,718,845 A (DROST et al.) 17 February 1998, see claim 10.	22

